

**A STANDARD ADDITIONS METHOD FOR THE MEASUREMENT OF SULFATE
PRODUCED DURING THE DETERMINATION OF SULFUR FORMS IN COAL
USING PERCHLORIC ACID**

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INTRODUCTION

A reaction scheme has been developed and tested at the Ames National Laboratory for the direct determination of the sulfur forms in coal (1). The variable oxidizing power of perchloric acid was used to selectively dissolve the various sulfur-containing components and convert them to sulfate for turbidimetric measurement. Sulfate was extracted with a perchloric acid solution boiling at 120°C. Pyrite was then determined by reacting the residue from the previous step with a perchloric acid solution boiling at 155°C. From the second residue, organic sulfur was oxidized with a 9:1 solution of concentrated perchloric acid and concentrated phosphoric acid boiling at 205°C. The phosphoric acid was used to prevent foaming of the mixture during the heating process. In all three steps, sulfur-containing gases were trapped in 15 percent hydrogen peroxide. Sulfate was then determined in the trap and in the aqueous solution by precipitation as barium sulfate followed by turbidimetric measurement. For some coals, the total sulfur recovered was slightly less than the total sulfur in the coal as determined by the ASTM procedure. Generally, the recoveries were on the order of 0.2 to 0.4 percent low out of a total sulfur content of about five percent. Possible explanations included: 1) the incomplete absorption of sulfur-containing gases by the neutral peroxide trap, 2) the dissolution of some organosulfur compounds at 155°C without being converted to the measurable sulfate form, and 3) the incomplete precipitation of barium sulfate during turbidimetric analysis due to the high acidity of the solutions.

It is possible that acidic gases, such as hydrogen sulfide or sulfur dioxide, might not be completely trapped by neutral hydrogen peroxide. Therefore, in order to test the first hypothesis, the oxidations were run using a peroxide trap made basic with ammonium hydroxide. Sulfate was then determined as before. The filtrate solution from the 155°C reaction was yellow-brown due to the dissolution of some organic material. Upon standing, a brown precipitate formed in these solutions. Dilution which occurred during filtration caused the perchloric acid to become more aqueous resulting in the precipitation of some organic material. To test the second hypothesis, the

precipitate was filtered and oxidized with perchloric acid boiling at 203°C in the Bethge apparatus with a peroxide trap. Sulfate was then measured by the turbidimetric method as above. Also, 5 mL aliquots from the 155°C filtrate were oxidized with hydrogen peroxide and again sulfate was measured turbidimetrically. To test the third hypothesis, sulfate was measured using a standard additions technique in which aliquots of a standard sodium sulfate solution were added to the test samples and sulfate was measured turbidimetrically.

EXPERIMENTAL

The coal used in this study was obtained from the Kentucky #9 seam and was ground to minus 100 mesh. A modified Bethge apparatus was used to maintain a constant boiling mixture. The Bethge apparatus has been described previously by McGowan and Markuszewski (2). The system was fitted with a gas trap, containing 15 percent hydrogen peroxide to collect sulfur-containing gases and convert them to sulfate, and with a nitrogen purge line.

A Note on Safety. The use of perchloric acid alone as an oxidizing agent for organic materials always poses a hazard. In this study, all reactions were performed in a hood and behind an explosion shield. In order to minimize the possibility of a fire or explosion, the authors urge that extreme caution be used anytime perchloric acid alone is used as an oxidizing agent. The authors recommend that reactions be performed at low temperatures first and that small amounts of organic material be employed.

Reaction Procedure. For each oxidation experiment, perchloric acid was added to the Bethge apparatus and the boiling point was adjusted to the desired temperature. By varying the initial amount of perchloric acid added, a final volume of approximately 50 mL was obtained. The boiling point could be increased by removing reflux condensate from the condenser. The boiling point could be decreased by adding water through the top of the apparatus. The 15 percent hydrogen peroxide trap was attached to the apparatus for each oxidation. Nitrogen was used as a purge gas. A weighed 1-g sample of coal was added to the flask. The sample was reacted with perchloric acid boiling at 120°C (actual reaction temperatures were noted in each step) for 45 min. The reaction mixture was filtered. The residue from the previous step was reacted with a perchloric acid solution boiling at 155°C for 1.5 hrs. The reaction mixture was filtered. The residue from above was reacted for 1 hr. with a 9:1 solution of concentrated perchloric acid and concentrated phosphoric acid boiling at 205°C. The phosphoric acid was added to inhibit foaming during the reaction. The reaction mixture was filtered and any residue was discarded. The filtrate from each of the three reactions was diluted to 250 mL. Each of the peroxide trap solutions was boiled to insure oxidation of the sulfur to sulfate and to reduce the volume to about 25 mL. The trap samples were then diluted to 50 mL. In each fraction, sulfate was determined by precipitation with barium and the turbidity of the resultant

barium sulfate suspension was measured spectrophotometrically using a calibration curve. For the solutions that were colored, the absorbance of the sample without the added barium was measured and subtracted from the absorbance of the test solutions. Sulfate in the coal sample was determined as sulfate in the filtrate, and sulfide in the coal was determined from the sulfate accumulated in the peroxide trap after the 120°C reaction. Pyritic sulfur was determined from the sulfate in the filtrate and peroxide trap after the reaction at 155°C. Organic sulfur was determined in the filtrate and in the peroxide trap after the reaction at 205°C. Total sulfur in the coal was determined by reacting 0.1-g samples of the coal with the perchloric acid and phosphoric acid mixture.

To test the first hypothesis, the above reaction scheme was performed using a 15 percent hydrogen peroxide trap which was made basic by the addition of 15 mL of concentrated ammonium hydroxide. To test the second hypothesis, the precipitate from the 155°C reaction was filtered and reacted with boiling concentrated perchloric acid. Sulfate was measured in the trap and in the reaction solution. Also, sulfate was measured using a 5.0 mL aliquot of the supernatant solution from the 155°C reaction. Another 5.0 mL aliquot from the same solution was then oxidized with 30 percent hydrogen peroxide, followed by the measurement of sulfate. To test the third hypothesis, a standard additions method was applied to the turbidimetric method used to measure sulfate. Amounts of 0.0, 0.1, 0.2 and 0.3 mL of a standard sodium sulfate solution which contained 0.62 g of sulfur/L were added to the appropriate volume of each solution, and the turbidity of each solution was measured as before.

RESULTS

The sulfate results from the oxidations run with the neutral trap on the Kentucky #9 coal appear in Table 1. The total sulfur, determined using the ASTM procedure, for this sample also appears in Table 1. The results with the basic trap, using a different split of this same sample of coal, appear in Table 2. The total sulfur for this sample was determined using the perchloric acid method (1). The sulfur recoveries, although still slightly low when using the basic hydrogen peroxide trap, were comparable to previous results, indicating that the neutral trap does an adequate job of absorbing the sulfur-containing gases. The results for the oxidations of the precipitate formed in the solutions from the 155°C reactions are presented in Table 3. No additional sulfur was recovered from these precipitates. The results for sulfur found in the solutions from the 155°C reactions, before and after oxidation with hydrogen peroxide, are presented in Table 4. Some additional sulfur (<0.1%) was recovered, although not enough to account for the low sulfur recoveries. Based on previous work (1-3), it was suspected that some sulfur might be lost in this step but that it would be small. It was interesting that additional sulfur was recovered from the aqueous solution and not from the precipitate formed from that solution. This would indicate that the dissolved

organosulfur compounds remained soluble while other organic compounds precipitated under the more aqueous conditions. Possibly the organosulfur compounds formed under these mildly oxidizing conditions were sulfonic acids and thus more soluble.

The sulfur recovery results using the standard additions technique on the Kentucky #9 coal appear in Table 5. The sulfur recoveries for this experiment were very close to the total sulfur in the coal. When these results were compared to the corresponding results for the same coal in Table 2, a slight increase was observed for each sulfur form (except sulfide). This indicated that there could be a systematic error in the turbidimetric technique used to measure sulfate. This error apparently involved the inability to match the conditions of the calibration curve to the matrix effects of the samples.

CONCLUSIONS

The neutral hydrogen peroxide trap is sufficient to trap sulfur-containing gases. Only a small amount of sulfur is converted to a soluble organosulfur compound at 155°C and is not measured as sulfate by the turbidimetric technique. Sulfur recoveries using the standard additions method are comparable to the total sulfur measured in the coal.

ACKNOWLEDGEMENTS

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TABLES

TABLE 1. Sulfur forms (in percent) determined for the Kentucky #9 coal using the perchloric acid procedure and a neutral trap

<u>SULFUR FORM</u>	1	2	3	4	AVG.
SULFATE	0.30	0.31	0.30	0.34	0.31
SULFIDE	0.02	0.03	0.01	0.00	0.02
PYRITE	2.81	2.70	2.80	2.83	2.79
ORGANIC	<u>1.36</u>	<u>1.41</u>	<u>1.24</u>	<u>1.47</u>	<u>1.37</u>
RECOVERY	4.49	4.45	4.35	4.64	4.48
TOTAL SULFUR (by the ASTM procedure)					4.86

TABLE 2. Sulfur forms (in percent) determined for the Kentucky #9 coal using the perchloric acid procedure and an ammoniacal trap

<u>SULFUR FORM</u>	1	2	3	4	AVG.
SULFATE	0.38	0.40	0.37	0.42	0.39
SULFIDE	0.14	0.01	0.03	-	0.06
PYRITE	2.69	2.91	2.91	2.46	2.74
ORGANIC	<u>1.32</u>	<u>1.31</u>	<u>1.56</u>	<u>1.48</u>	<u>1.42</u>
RECOVERY	4.53	4.63	4.87	4.36	4.60
TOTAL SULFUR (by the perchloric/phosphoric acid procedure)					4.96

Table 3. Sulfur (in percent) in precipitates from the solutions after the 155°C reactions

<u>FRACTION FROM</u>	1	2	3
FILTRATE	0.00	0.00	0.00
TRAP	0.00	0.00	0.00

TABLE 4. Sulfur (in percent) recovered from solutions after the 155°C reactions

<u>SOLUTION</u>	1	2	3
BEFORE H ₂ O ₂ OXIDATION	0.37	0.62	0.53
AFTER H ₂ O ₂ OXIDATION	<u>0.46</u>	<u>0.67</u>	<u>0.61</u>
ADDITIONAL SULFUR	0.09	0.05	0.08

TABLE 5. Sulfur forms (in percent) determined for the Kentucky #9 coal when sulfate was measured using standard additions

<u>SULFUR FORM</u>	1	2	AVG.
SULFATE	0.69	0.39	0.54
SULFIDE	0.01	0.01	0.01
PYRITE	2.81	2.91	2.86
ORGANIC	<u>1.52</u>	<u>1.56</u>	<u>1.54</u>
RECOVERY	5.03	4.87	4.95
TOTAL SULFUR (by the perchloric/phosphoric acid procedure)	4.96		

QUANTITATIVE ANALYSIS OF SULFUR FUNCTIONAL FORMS AND REACTIONS BY XAFS SPECTROSCOPY

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INTRODUCTION

Recently, significant progress has been made in quantifying the measurement of different functional forms of sulfur in coal using X-ray absorption fine structure (XAFS) spectroscopy. As discussed in detail elsewhere, three methods of analyzing the X-ray absorption near edge structure (XANES) have been proposed.^[1-6] In the current paper, we will briefly review the method developed by our group, which consists of direct least squares analysis of the XANES and conversion of the photoelectron $s \Rightarrow p$ transition peak areas into sulfur percentages using empirically determined calibration constants.^[3] A number of applications of this method will be briefly summarized, including investigation of sulfur forms as a function of rank,^[3] in situ studies of sulfur transformations during pyrolysis and oxidation,^[7-9] and chemical and biological reactions of sulfur in coal.^[10]

EXPERIMENTAL PROCEDURES

Experimental details are discussed elsewhere.^[11-3,7-10] All XAFS experiments were conducted in the x-ray fluorescent mode^[11] at beamline X-19A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The in situ experiments were carried using an XAFS compatible high temperature cell with the sample under flowing helium, hydrogen, or helium-5% oxygen at temperatures ranging from 200 to 600°C.^[7-9] An XAFS spectrum was acquired at each temperature, making the pyrolysis and oxidation treatments fairly slow.

The suite of coals examined have included the Argonne Premium Coal Sample Bank (APCSB) coals, numerous additional whole coals, a suite of maceral separates, and a variety of chemically and biologically treated samples.

RESULTS AND DISCUSSION

Typical least squares analyzed XANES spectra are shown in Figure 1. The lower spectra in Figure 1 are room temperature spectra of an APCSB Illinois No. 6 coal and a low-rank Victorian brown coal (Glencoe). The upper half of Figure 1 shows high temperature spectra obtained in situ during oxidation of the Glencoe coal at 450°C and pyrolysis of the APCSB Illinois No. 6 coal at 600°C. As discussed elsewhere,^[3] the least squares analysis method fits the XANES spectra to a series of photoelectron $s \Rightarrow p$ transition peaks using 50:50 Lorentzian:Gaussian peak shapes, and to one or two arctangent step functions representing the photoelectron transition to the continuum. Because the major sulfur forms in coal and coal derivatives have characteristic $s \Rightarrow p$ transition energies, the $s \Rightarrow p$ peak associated with each sulfur form can be identified. It is found that the $s \Rightarrow p$ transition energy increases with valence, as follows: pyrrhotite, -1.5 eV; pyrite, -0.5 eV; elemental sulfur, 0.0 eV; organic disulfide, 0.2 eV;

organic sulfide, 0.7 eV; thiophenic sulfur, 1.3 - 1.8 eV; sulfoxide, 3.4 eV; sulfone, 7.5 eV; and sulfate, 9.9 - 10.1 eV.¹ Once the $s \Rightarrow p$ peak areas have been determined from the least squares fit, empirically determined calibration constants are used to convert them to sulfur percentages.^[3]

The results for the APCSB coals and a number of additional whole coals are summarized in Table 1. A number of points are worth noting. First, the only APCSB coal that exhibits significant sulfur oxidation is the Beulah (ND) lignite, which contains a sulfate component believed to be gypsum. Second, the pyritic sulfur percentages derived from XANES agree reasonably well with those derived from Mössbauer spectroscopy.^[11,12] Third, the percentage of organic sulfur that is sulfidic increases with decreasing rank as shown in Figure 2, although thiophenic sulfur was the dominant organic sulfur form for all coals examined. The thiophenic and sulfidic percentages determined for the APCSB coals agree fairly well with those determined by Gorbaty et al.^[6] using a third derivative method of analyzing the XANES spectra.

We have also completed XANES analysis of a suite of maceral separates, and find that the sulfidic content of exinite is consistently higher than that of vitrinite or inertinite.^[3] Additionally, it is found that the inertinite separates frequently contain fairly high percentages of pyrite, indicating that coal particles containing fine included pyrite are often incorporated into the specific gravity range corresponding to inertinite during density gradient centrifugation.

Several coals have been investigated by high temperature *in situ* XAFS spectroscopy conducted during pyrolysis and oxidation. The results, which are discussed in more detail elsewhere,^[7-9] are summarized in Figure 3. Briefly, the organic sulfide component decreases above approximately 300°C, under both pyrolysis and oxidation conditions, with the sulfide percentage falling to about half of its initial value on reaching 500 to 600°C. The disulfide percentage for the Australian brown coal begins to decrease between 200 and 300°C, reaching approximately one fourth of its original value at 500 to 600°C. The Illinois #6 data shows that pyrite transforms to pyrrhotite during pyrolysis and to pyrrhotite and sulfate during oxidation, above approximately 400°C. During oxidation of the Glencoe coal, a sulfate phase is also formed, but it is unlikely to be an iron sulfate since the coal contains no pyrite and very little iron. Either an organic sulfate or calcium sulfate are possibilities. During pyrolysis of the Glencoe coal, a negative valence (~ -2) sulfur species is observed to form and increase to approximately 40% of the total sulfur at 500°C. A double-bonded C-S compound, such as a thio ketone, or calcium sulfide, are possible candidates.

There is considerable interest in the effects of various chemical and biological reactions on sulfur in coal. We have examined the effects of several such treatments on a number of coals using XANES spectroscopy. A more detailed summary of the results is available in a forthcoming paper [10]. For the current article we will summarize some recent data obtained on the use of perchloroethylene (PCE) for removal of sulfur from coal. In this treatment,^[13] coal is treated with a five-fold excess of PCE at close to its boiling point (125°C) for no more than 30 minutes, in which time a significant reduction (up to 50%) in the organic sulfur is claimed to occur. The exact mechanism has not yet been clarified, but the observation has been made^[13] that the sulfur removed from the coal by PCE can be readily extracted in the form of elemental sulfur. However, this focus on elemental sulfur has lead others^[14,15] to criticize this method by claiming the PCE is only removing the elemental sulfur already present in the coal. As

¹The energy of the elemental sulfur $s \Rightarrow p$ transition, which is actually approximately 2472 eV, is chosen to be 0, and all other energies are measured relative to that standard.

oxidation of pyrite is the principal and possibly only method by which elemental sulfur can come to be present in the coal.^[14,16,17] It has been postulated that the PCE method will only be effective with oxidized coals.

A number of samples before and after treatment with PCE have now been examined with both XAFS and Mössbauer spectroscopies. The Mössbauer results^[10] show that the amounts of pyrite in these samples are basically unaltered by the PCE treatment. Hence, the pyritic sulfur in these coals is *not* affected by the PCE treatment.

The sulfur K-edge XANES data for the Upper Freeport coal before and after PCE treatment are shown in Figure 4 and the results on the sulfur forms derived from the least-squares fitting are summarized in Table 2. The XANES results for Freeport coal clearly show a major reduction in at least one form of sulfur. Based on the peak position (0.3 eV) of the peak that disappears, it is difficult to reconcile it with an organic sulfide, the peaks of which occur typically at around 0.7 eV. After the PCE treatment, there is a peak located at 0.7 eV, which is approximately 30% of the intensity of the peak present before PCE treatment. This peak position is compatible with an organic sulfide. Hence we interpret the large peak present in the XANES spectrum of the sample before PCE treatment as a composite peak consisting of contributions from both elemental sulfur and organic sulfide. This would also account for its position intermediate between that for sulfide (0.7 eV) and elemental sulfur (0.0 eV). Such an interpretation strongly suggests that the peak removed is due primarily to elemental sulfur, and based on the XANES analysis, we estimate that about 0.6 - 0.7 wt% sulfur is removed in this form. The value was later confirmed independently by D. Buchanan (E. Illinois University).

It should also be noted that there appears also to be some decrease in the amount of thiophenic sulfur (≈ 0.15 wt%) based on the total sulfur value estimated for the coal (3.2 wt%) after elemental sulfur removal. However, this amount is within the experimental uncertainty of the technique and may not be significant.

A sample of Indiana #5 coal also exhibited distinct changes with the 30-minute boiling PCE treatment. The organic sulfur forms, calculated from the peak areas in the XANES spectrum and identified on the basis of their peak position, are summarized in Table 2. It would appear that the sulfur species in the Indiana #5 that are reduced by the PCE treatment are elemental sulfur and, to a lesser extent, possibly also the organic sulfide species. However, such a small change is within the estimated experimental errors of the XANES measurement.

A number of other coals subjected to treatment with boiling PCE exhibit essentially the same spectrum after treatment as before and therefore do not show any significant preferential removal of different sulfur forms. Such coals investigated to date include an Ohio #5/#6 coal, an unoxidized Illinois #6 coal from the Argonne Premium sample bank, an oxidized Illinois coal obtained from Prof. D. Buchanan (E. Illinois University), and high sulfur (5.7 wt%) Australian brown coal (Glencoe) that contained a large organic sulfide content and virtually no pyritic sulfur (<0.2 wt.%).

SUMMARY AND CONCLUSIONS

Least squares analysis of sulfur K-edge XANES spectra is a powerful method for quantitative analysis of the functional forms of sulfur in coal and related materials. Thiophenic sulfur is the dominant organic sulfur form observed in all of the coals we have examined, but sulfidic sulfur increases significantly with decreasing rank. Sulfidic sulfur is higher in exinite

maceral separates than in vitrinite or inertinite. Pyritic sulfur measured by XANES agrees with that determined by Mössbauer spectroscopy.

The reactions of different sulfur forms during chemical, biological, or thermal treatment can be quantitatively followed using XANES spectroscopy. Quantitative in situ XANES measurements during coal pyrolysis and oxidation have been carried out at temperatures up to 600°C.

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TABLE 1: Derived percentages for forms of sulfur in Argonne Premium coals and several additional coals.

Argonne Premium Coal Sample	Wt% Total Sulfur	Sulfur Forms, %					
		Pyrite	Sulfide	Thioph.	Sulfox.	Sulfone	Sulfate
Pocahontas #3, VA	0.66	24	0	75	0	1	0
Upp. Freeport, PA	2.32	62	6	33	0	1	0
Pittsburgh #8, PA	2.19	52	13	35	0	1	0
Lewis-Stock., WV	0.71	26	16	56	1	1	0
Blind Canyon, UT	0.62	40	15	46	0	0	0
Illinois #6, IL	4.83	48	19	33	0	0	0
Wyodak-Anders., WY	0.63	24	29	46	0	0	0
Beulah, ND (fresh)	0.80	29	28	30	2	0	12
Beulah, ND (2nd.)	0.80	37	24	30	2	0	7
Additional Coals							
Illinois #6, IBC-101	3.08	34	21	38	3	4	1
Wyodak (micronized)	n.r.	27	25	45	0	0	3
Texas Lignite	n.r.	49	18	30	0	1	2
Glencoe brown coal	5.73	0	44*	55	0	0	1

*Sulfide contribution is 27%; disulfide (\pm polysulfide) contribution is 17%.

TABLE 2: Derived percentages for forms of sulfur in coals treated with PCE.

Coal Sample treated with PCE	Wt% Total Sulfur	Sulfur Forms, %					
		Pyrite	Sulfur	Sulfide	Thioph.	Sulfone	Sulfate
Freeport, before	3.75	1.8	0.65	0.25	0.85	0.0	0.2
Freeport, after	3.10*	1.9	0.0	0.25	0.7	0.0	0.25
Indiana #5, before	2.50	0.85	0.35	0.4	0.4	0.05	0.45
Indiana #5, in situ	(2.25)	(0.85)	0.2	0.3	0.4	0.05	0.45
Indiana #5, after	1.90	0.85	0.0	0.25	0.4	0.05	0.35

Pyritic sulfur values from Mössbauer spectroscopy.

*Total sulfur estimated as (Total sulfur of coal before - sulfur removed)
Values in () are estimated values, assuming no change in pyritic sulfur.

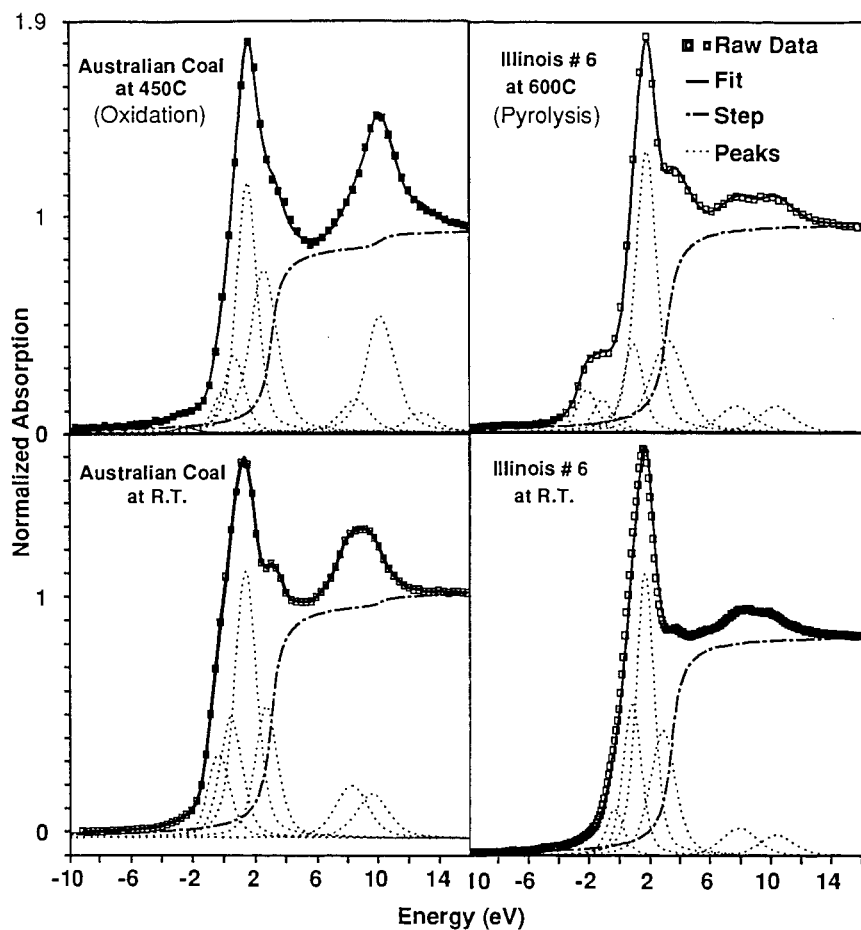


Figure 1. (Right) Fitted XANES spectra of the Illinois # 6 coal obtained at room temperature and at 600C in helium. (Left) Fitted XANES of Australian brown coal at room temperature and at 450C in a helium-oxygen mixture.

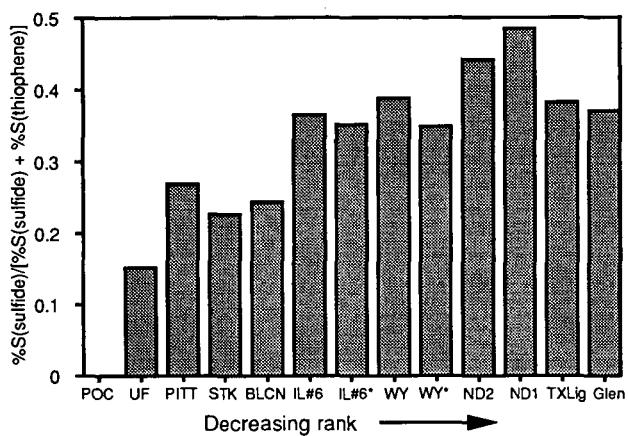


Figure 2: %S(sulfide)/[%S(sulfide)+%S(thiophene)] ratio plotted as a function of rank for the Argonne Premium Coal samples and a number of additional coals. The samples marked with a * are float samples of Illinois #6 and Wyodak coal obtained from Southern Illinois University. Results for two samples of APCS Beulah-Zap, ND1 and ND2, are also shown.

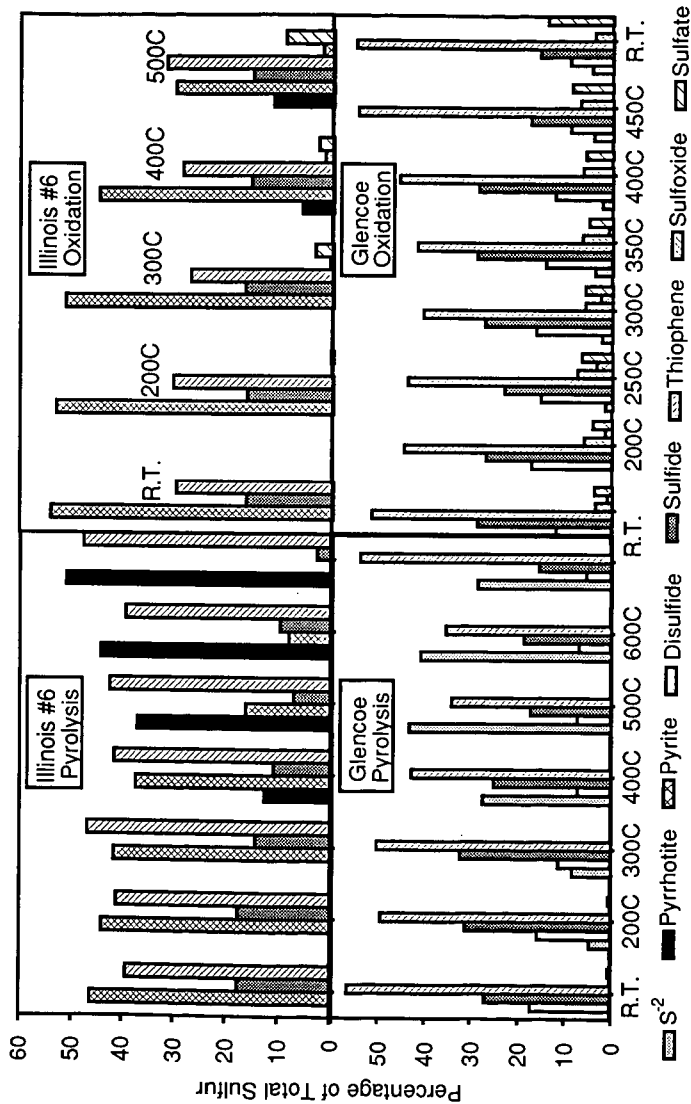


Figure 3. Percentage of sulfur in various functional forms determined by in situ XAFS spectroscopy as a function of temperature for: Illinois # 6-Pyrolysis (upper left); Illinois # 6-oxidation (upper right); Glencoe-Pyrolysis (lower left); Glencoe-oxidation (lower right).

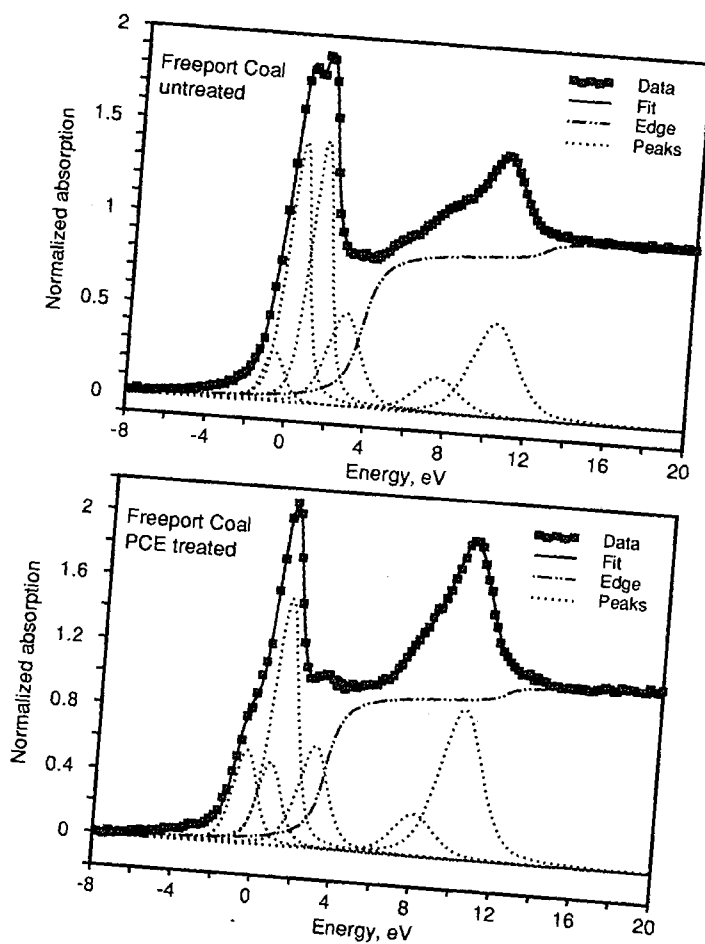


Figure 4: Least-squares fitted sulfur K-edge XANES spectra of Freeport coal before and after treatment with perchloroethylene (PCE).

REACTIVITY OF OXIDIZED ORGANIC SULFUR FORMS IN COAL

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1. INTRODUCTION

Recent work has shown that it is possible to distinguish and quantify the different organic sulfur types in coal using X-Ray Photoelectron Spectroscopy (XPS) [1-3] and X-Ray Absorption Near Edge Structure Spectroscopy XANES [3-6]. These methods have been employed in the study of fresh coals of different rank and to follow the transformation of organic sulfur under mild pyrolysis conditions ($T = 400^{\circ}\text{C}$) [7]. The characterization of oxidized organic sulfur forms resulting from mild coal oxidation [2, 8-11] and the subsequent thermal reactivity of these oxidized sulfur forms have not been as extensively explored. The nature of oxidized organic sulfur forms can yield insight into the forms initially present [12]. Initial work with Rasa coal showed that sulfide sulfur forms are converted to oxidized forms while thiophenic forms were mostly unreacted [2]. This paper extends that work to other coals and explores the subsequent thermal reactivity of the oxidized organic sulfur forms.

2. EXPERIMENTAL

The procedures for obtaining XPS and XANES spectra have been discussed elsewhere [1,3]. Pyrolysis with GC gas product analysis were done in a quartz reactor contained within a furnace. The details of these experimental arrangements have been previously described [7,13]. Heating rates were on the order of $0.5^{\circ}\text{C}/\text{min}$ up to 400°C . The temperature and heating conditions were chosen because little of the ultimate amount of hydrocarbons in the volatile matter is released, while much of the H_2S and SO_2 evolve from low rank coals. Spanish lignite (Mequinenza), New Zealand (Charming Creek) and Rasa coal were chosen for study because of the unusually high amounts of organically bound sulfur and unusually low levels of pyritic sulfur [14-16] present. Oxidation was done in the dark, in air (ambient relative humidity 60%) and in an oven kept at 125°C for 5 days.

3. RESULTS and DISCUSSION

The oxidation conditions were chosen because it was found in other coal oxidation studies that the relative rate of total organic oxidation corresponded closely with that of oxidized organic sulfur during the first 5 days at 125°C [10]. Also, the oxidation rates at 125°C can be related kinetically to those that occur near ambient conditions [10,11]. There is roughly two orders of magnitude acceleration of time at 125°C relative to room temperature. Table I shows the XPS quantitative speciation of sulfur forms in the fresh and oxidized coals. Note that sulfides, mercaptans and disulfides are included as "sulfide" in Table I. These results show that a large fraction of the sulfides initially present in the fresh coals is converted to oxidized forms, while thiophenic forms are relatively stable under these mild conditions. For Rasa coal, the dominant oxidation product was identified to be sulfonic acid. For the other

coals, sulfones and sulfoxides are the major oxidation products. Pure compound work has shown that sulfonic acids can arise from the oxidation of disulfides or mercaptans, while sulfoxides and sulfones result from oxidation of sulfides [17,18]. It is apparent from the data above for the Spanish and New Zealand coals that sulfides are converted to sulfoxides and sulfones. For Rasa coal, the evidence supports the speculation that disulfides are the precursors of sulfonic acids. In support of this, the "sulfidic" value for the fresh Spanish coal contains a 15% contribution from an XPS feature associated with mercaptans [7]. This feature does not decrease upon oxidation, nor is sulfonic acid a major product of oxidation. Mercaptans were not identified in fresh Rasa and New Zealand coals. Thus disulfides appear to be the most likely precursors of sulfonic acids in oxidized Rasa coal.

It has been shown that aliphatic sulfur forms decompose to H_2S with some conversion to aromatic forms upon mild pyrolysis [7]. Table II shows the amount of H_2S and SO_2 generated upon pyrolysis for 5 minutes at $400^\circ C$, expressed on an atomic S/C basis. Data in Table II show that for fresh Rasa coal sulfide sulfur preferentially decomposes to H_2S , while H_2S formation and conversion to aromatic forms takes place with New Zealand and Spanish coal. The thermal reactivity of the oxidized coal samples shows considerably less H_2S product than the fresh coals. The relative loss in H_2S production roughly tracks the relative loss of sulfide forms in each coal. This supports the view that sulfide sulfur forms are preferentially converted upon oxidation. Data in Table II show that the oxidized organic sulfur forms are lost as SO_2 upon mild pyrolysis. Rasa coal is the most reactive with the appearance of 43% of the oxidized forms as SO_2 . For the New Zealand and Spanish coals 7% and 18% respectively of bound oxidized sulfur appeared as SO_2 by this analysis.

These results together with XPS and XANES analysis of the low temperature chars indicate that most of the sulfur present as sulfoxides and sulfones formed during low temperature oxidation is retained in the coal after low temperature pyrolysis. As found for these initial coals [7,14] little sulfide sulfur remains after pyrolysis. While previous work demonstrated that the relative level of aliphatic or "sulfide" sulfur decreases with increasing coal rank [3,7] the present work shows that there can be significant differences in the nature of the components that comprise "sulfide" sulfur. Distinctions can be made on the basis of products following mild oxidation and subsequent thermal reactivity of the oxidized coals.

4. CONCLUSIONS

Sulfide sulfur forms are converted to oxidized forms during mild coal oxidation. Thiophenic forms are largely unreactive. The oxidation products of Spanish lignite and New Zealand coal were mostly sulfones and sulfoxides while Rasa coal gave sulfonic acids. TPD and reactor studies show that the conversion of organic sulfides to oxidized products causes a large decrease in H_2S production upon pyrolysis. A portion of the oxidized organic sulfur forms are lost during low temperature pyrolysis as SO_2 . Rasa coal is the most reactive and the amount of SO_2 produced corresponds to 43% of the oxidized species originally present. XPS analysis of oxidized Rasa coal after pyrolysis shows sulfonic acids represent most of the loss. A much smaller fraction of the oxidized sulfur forms initially present in the other coals yield SO_2 upon low temperature pyrolysis. TPD, XPS and XANES results indicate that most of the sulfur initially present as sulfoxides and sulfones is retained in the coal after low temperature pyrolysis.

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Table I XPS analysis of sulphur before and after oxidation at 125°C

Sample	Mole per cent				
	Sulfide	Thiophene	Sulfoxide	Sulfone	Sulfonic Acid
Rasa Initial	26	70	1	1	2
Rasa Oxidized	7	69	4	8	12
Spanish Initial	66	34	0	0	0
Spanish Oxidized	38	42	5	8	4
N.Z. Initial	38	62	0	0	0
N.Z. Oxidized	13	67	8	8	4

Table II Amount of oxide and sulfidic components and the subsequent amount of H₂S and SO₂ produced upon pyrolysis

Sample	Atom Ratio S/C (x100)			
	XPS Sulfide	H ₂ S Pyrolysis	XPS Oxides	SO ₂ Pyrolysis
Rasa Initial	1.83	1.53	0.24	0
Rasa Oxidized	0.42	0.18	1.43	0.61
Spanish Initial	4.25	1.49	0	0
Spanish Oxidized	2.64	0.89	1.18	0.21
N.Z. Initial	1.06	0.17	0	0
N.Z. Oxidized	0.35	0.08	0.56	0.04

ADVANCES IN COAL CHARACTERIZATION BY PROGRAMMED-TEMPERATURE OXIDATION

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ABSTRACT

This paper describes the current status for the characterization of coal by controlled-atmosphere programmed-temperature oxidation (CAPTO). Distinctive gas evolution patterns are observed among coals of different rank and between raw and treated coals. In addition to two resolved SO₂ peaks, assignable to the oxidation of pyrite and the decomposition of sulfate, two others, assignable to organic structures in the coals, are observed.

INTRODUCTION

Interest continues to be strong in methods to reduce the levels of SO₂ and NO_x in the atmosphere as a control strategy for acid deposition. Retrofit technologies (pre- and post-combustion and combustion modification) used singularly or in combination offer the coal-fired utilities a potential route to meet state and federal regulations while limiting capital expenditures in comparison to repowering technologies. Conventional physical cleaning methods result in some inorganic sulfur (pyritic and sulfatic) reductions from coal while the advanced physical coal cleaning procedures under development offer the potential for significant pyrite reduction. Physical cleaning along with coal switching and post-combustion scrubbing techniques are the primary routes currently in use by the utilities in an attempt to meet air emission regulations.

Numerous precombustion chemical beneficiation procedures were developed in the 1970's that removed most of the inorganic sulfur (pyritic and sulfatic) and some of the organic sulfur from coal. Morrison¹ provides an excellent review of these technologies. Bioprocessing as a route for sulfur removal from coal is now under intensive study². Continued development of advanced coal cleaning technologies generates a need for suitable analytical techniques to monitor progress of the work.

The ASTM organic sulfur determination for coal is based upon the difference between the total sulfur analysis and the sulfatic and pyritic sulfur analyses of coal (Method D2492). The method works well for most untreated coals. However, the presence or formation of certain inorganic sulfur species in coals, particularly treated coals, that are partially insoluble in hydrochloric or nitric acid, results in a higher reported value for organic sulfur. This limitation presents a serious problem to all laboratories involved in coal desulfurization and other clean coal research. A number of routes to characterize the sulfur distribution in coals have been, and continue to be, studied. Friedman³ recently presented a critical review of sulfur analyses of coal and Stock et al.⁴ reviewed methods to determine sulfur distribution in American bituminous coals. A generally accepted, routine method to distinguish between the organic-sulfur functional groups or to classify the organic sulfur present in treated and untreated coals is vital to those involved in clean coal research.

Reductive and oxidative techniques have been developed as potential routes to classify the sulfur types present in raw and treated coals. Yergy et al.,

using a reductive approach, monitored the hydrogen sulfide evolved from a linear increase in temperature and noted five different types of hydrogen-induced sulfur release. Additionally, Attar⁸ described a non-isothermal kinetic method for estimation of the organic sulfur functional groups in coal. Majchrowicz et al.⁹ recently described an automated approach to the temperature programmed reduction route. However, these reductive approaches do not respond to much of the organic sulfur in coal and cannot be utilized to give any reliable quantitative information for the inorganic, organic, and total sulfur in coal.

Numerous groups have also investigated oxidation as a route to identify sulfur species. Chantret¹⁰, monitored airflow through a differential thermal analysis chamber for SO₂ and CO₂. Temperature rise in an absorbent, lead dioxide for SO₂, and Ascarite for CO₂, was used to detect the presence of the gases. LaCount et al.¹¹ using a thermal oxidative technique coupled with evolved gas analysis, described a route to qualitatively and quantitatively^{12,13} characterize the sulfur, carbon, and hydrogen in coals and treated coals. A coal sample thoroughly dispersed in an inert diluent used to control the exothermic oxidation reactions was exposed simultaneously to a linear increase in temperature and an oxygen/argon flow. Continuous measurement of the concentration of gases evolved from the sample provided a concentration/time or temperature profile for each evolved gas. By use of model compounds and polymeric substances, each SO₂ evolution maxima produced from coal was eventually related to the probable structural type causing the maxima. Integration of the profiles provided an estimate of the sulfur forms and the total sulfur in the coal sample. Total sulfur values were in good agreement with those obtained from ASTM analyses. However, significant overlap of the SO₂ evolution maxima resulting from pyrite and organic sulfur prohibited quantitative estimation of the sulfur forms in raw coals.

Boudou et al.¹⁴ briefly reviewed work in programmed pyrolysis, reduction, and oxidation. Using procedures similar to Chantret's and several other methods, they studied the sulfur species in several high organic sulfur coals.

Calkins¹⁵ described pyrolysis experiments directed toward the determination of organic-sulfur-containing structures in coal and briefly reviewed work in this area. Pixari et al.¹⁶ studied oxidative pyroanalysis as a route to the elemental analysis for the volatile and nonvolatile fractions of coals.

Other routes for a direct determination of organic sulfur in coal have been investigated. Some of these involve the electron microprobe^{17,18}, the scanning electron microscope¹⁹, or the transmission electron microscope²⁰. The equipment involved is costly and variations in the organic sulfur content in coal requires averaging over a number of sites in each sample. Huffman et al.²¹ investigated the molecular structure of organic sulfur in coal macerals by X-ray absorption fine structure (XAFS) spectroscopy. However, additional work is required on model systems to clarify ambiguities in the interpretation of the XAFS data.

A step-wise procedure using perchloric acid for determination of sulfate, sulfide, pyrite, and organic sulfur in a single coal sample has been reported²². However, the procedure is tedious and probably not suitable for routine analyses.

DISCUSSION

This paper describes recent improvements in oxidation conditions and in the detection system of the controlled-atmosphere, programmed-temperature oxidation (CAPTO) apparatus previously described⁹. The effort is directed toward development of methodology to obtain well resolved evolution profiles that will enhance our understanding of the nature of sulfur present in coal. This knowledge is basic to the development of improved technology for sulfur removal from coals and for selecting those coals which have the greatest

beneficiation potential. The unit also offers potential as a one-step direct analysis route for the inorganic, organic, and total sulfur present in untreated and treated coals.

Several current applications utilizing a partially modified instrument are discussed. A complete description of the totally redesigned CAPTO instrument/method (patent pending) will be presented elsewhere.

INSTRUMENT MODIFICATIONS AND METHOD

Portions of the system shown in *Figure 1* have been previously described¹³. An FTIR spectrometer is used as a detector for analysis of the SO₂, CO₂, H₂O, and NO₂ formed instead of the nondispersive infrared analyzers formerly used.

The CAPTO technique is used to analyze coals, treated coals and other high molecular weight substances reduced to a particle top size of -60 mesh, or smaller. The sample is thoroughly dispersed in a diluent (to reduce exotherms that occur during oxidation) and exposed simultaneously to a linear increase in temperature and to an oxygen/argon flow. The oxidized gases are monitored continuously and intermittent evolution maxima are observed for SO₂, CO₂, H₂O, and NO₂ as the oxidation proceeds. If the SO₂ evolution maxima are well resolved, a quantitative estimation of the sulfur types present in the sample can be obtained. However, the oxidation conditions used in previous work (diluent, 10% O₂ in argon, and a temperature ramp of 2 - 5°C/min.) resulted in overlap between the evolution maxima detected from pyritic sulfur and that from the second major occurrence of organic sulfur in coal.

In order to improve the oxidative technique, experiments were completed with the reaction parameters (temperature ramp, oxidant flow, and oxygen concentration) varied systematically. Optimum temperature ramp and flow were established. Using these conditions the programmed temperature oxidation of coal samples was studied as a function of oxygen concentration.

A series of CAPTO experiments were performed with ROM Illinois No. 6 coal. A different oxygen concentration was used in each experiment. The oxygen concentration in argon was varied from 4% to 16% in 2% increments. No improvement in resolution of the SO₂ evolution profile was noted. In fact, the pyritic and second organic SO₂ evolution maxima showed a decrease in resolution with increasing oxygen concentration. Careful measurement of the pyritic SO₂ evolution maxima revealed a slight shift to higher temperatures with increasing oxygen concentration (e.g. 4% - 430°C; 10% - 435°C). A CAPTO experiment using 20% oxygen resulted in one SO₂ evolution maxima at 445°C for the pyritic and aromatic sulfur.

Although loss of oxidative selectivity between the two major occurrences of CO₂ and SO₂ derived from organic structures in the coal was a concern, CAPTO experiments were completed using pure oxygen. The results (*Figure 2*) show that the oxidative selectivity between the first (290°C) and second (420°C) major evolutions of SO₂ from organic structures is retained and, importantly, the pyritic sulfur is oxidized at a higher temperature (478°C) than the organic sulfur. *Figure 2* also shows SO₂ evolution due to decomposition of iron sulfate at 585°C.

Previously, ¹³C CP-MAS n.m.r. work¹³ was completed on coal samples both before and after a CAPTO experiment that was terminated at 400°C. The n.m.r. spectrum prior to the experiment clearly indicated the presence of aromatic structures and nonaromatic structures (*f_a* = 0.69). After the sample was exposed to CAPTO conditions up to 400°C, the spectrum revealed an essentially unchanged aromatic region; however, the nonaromatic region had been almost totally eliminated (*f_a* = 0.87). Thus, the lower temperature CO₂ and SO₂ evolutions resulting from organic structures were attributed to carbon and sulfur lost primarily from oxidation of nonaromatic coal structures, and the CO₂ and SO₂

evolutions from organic structures above 400°C were attributed primarily to carbon and sulfur lost during oxidation of the aromatic coal matrix. We still believe this to be a generally valid premise. However, as noted in our earlier work¹³, stable aryl sulfides and sulfones oxidize above 400°C and would be included in addition to thiophenic structures in what we term "aromatic".

APPLICATION OF CAPTO TO MICROBIAL TREATED COAL

An example in which both CO₂ and SO₂ evolution profiles are important in characterizing a coal/treated coal is shown below. A -200 mesh Illinois No. 6 ROM coal was treated with a mixed consortium of *Thiobacillus ferrooxidans* for 15 days at 30 - 35°C (CO₂ purge). The CAPTO results from the untreated and treated coal are shown in Figures 3 and 4. The SO₂ evolution profile for the untreated coal shows the presence of temperature maxima for nonaromatic sulfur (290°C), aromatic sulfur (410°C), pyritic sulfur (478°C), and sulfate (590°C). This sulfur profile is consistent with other Illinois No. 6 raw coal samples tested in our laboratory. The SO₂ evolution profile from the treated coal shows that (1) the nonaromatic SO₂ evolution temperature is unchanged and (2) the pyritic sulfur and sulfate have been removed. However, a portion of the aromatic sulfur has been oxidized at 385°C, 25°C below the oxidation temperature of aromatic sulfur in the untreated coal.

The CO₂ evolution profile for the untreated coal (Figure 4) shows temperature maxima for nonaromatic carbon oxidation at 290°C and aromatic carbon oxidation at 420°C. The CO₂ evolution profile for the treated coal shows the oxidation temperature of the nonaromatic carbon to be unchanged, but a portion of the aromatic carbon is oxidized at 390°C, 30°C below that of the untreated coal.

The CAPTO technique is sensitive to changes in coal structure and sulfur content resulting from the bioprocessing of coal.

APPLICATION OF CAPTO TO MOLTEN CAUSTIC LEACHING

A Pittsburgh Seam (ROM) coal (Ohio No. 8) from Belmont County, Ohio was thoroughly mixed with an inorganic diluent, and simultaneously subjected to an oxygen flow and a programmed linear increase in temperature. Pyrite oxidation occurs after the organic sulfur has been oxidized as shown in Figure 5. This sample of Pittsburgh Seam coal was taken from a feed coal used in a molten caustic leaching treatment. The CO₂ and H₂O evolutions are also shown in Figure 5.

The products resulting from two different molten caustic treatments were also examined oxidatively under the same CAPTO conditions as the feed coal. The results are shown in Figures 6 and 7. The molten caustic leached product used to produce the CAPTO results of Figure 6 had been treated with 1:1 KOH/NaOH, 2:1 caustic/coal at approximately 438°C (kiln outside wall temperature). Essentially all of the pyrite and iron sulfate have been removed by the caustic treatment. A small broad SO₂ evolution peak centered at 330°C is present indicating that the nonaromatic/aromatic sulfur content has been significantly reduced compared to that of the feed coal shown in Figure 5.

The molten caustic leached product used to obtain the CAPTO results shown in Figure 7 had been treated with NaOH at a caustic to coal ratio of 2:1 at approximately 415°C (kiln outside wall temperature). Sulfur dioxide from pyrite and iron sulfate do not appear in the profile. The aromatic sulfur has been markedly reduced in this sample; however, a small residual aromatic sulfur evolution centered at 415°C is noted. The nonaromatic sulfur has been removed to a lesser degree and a small SO₂ evolution peak centered at 290°C is noted. These results confirm our earlier findings¹³ that the molten caustic treatment in this temperature range removes more aromatic sulfur than nonaromatic sulfur.

The CO₂ and H₂O evolution profiles have also been recorded and plotted in *Figures 6 and 7*. This information is routinely obtained from the oxidative degradations and provides a route to continuously measure the C/H ratio as oxidation proceeds. Thus, it is of value beyond the C/H ratio obtained simply from total carbon and hydrogen analyses. Note the differences between the CO₂ evolution profiles in *Figures 6 and 7*. A shoulder denoting oxidation of nonaromatic carbon at 310°C is present in *Figure 7*. *Figure 6* (results of treatment at 438°C) shows less nonaromatic carbon compared to the coal treated at 415°C (*Figure 7*). *Figure 7* also shows considerably more water resulting from oxidation of nonaromatic hydrogen than *Figure 6*. The molten caustic product (*Figure 6*) formed at 438°C appears to be much more "charlike" than the product (*Figure 7*) formed at 415°C. One would expect the product formed at 415°C to have better combustion properties than the product formed at 438°C.

Measurement of CO₂ evolved as the oxidative degradation proceeds also helps to better define the point at which the SO₂ produced must be derived from a noncarbon source. The CAPTO technique is sensitive to changes in coal structure and sulfur content resulting from changes in molten caustic leaching conditions.

CAPTO MODEL SYSTEMS

The redesigned CAPTO apparatus utilizes a high oxygen concentration flow. A change in concentration from 10% oxygen in argon to 100% oxygen is associated with an increase in the pyrite oxidation temperature from 430°C to 478°C. While the oxidative selectivity between the two major occurrences of CO₂ and SO₂ from organic carbon and sulfur has been retained, the oxidation temperatures have decreased. Additionally, one must expect that the oxidation temperatures of standards and model systems originally used to establish a correlation between their oxidation temperatures and the oxidation profile of coals will change. Accordingly, the key standards and model systems are being oxidized under the new conditions. The oxidation results obtained to date are compared in *Table 1*. The SO₂ evolution temperatures of the model systems under the new conditions are consistent with the coal assignments.

CONCLUSIONS

Using high oxygen concentrations, the CAPTO SO₂ evolution peaks due to the oxidation of the aromatic and pyritic sulfur are sufficiently resolved so that small differences in the amounts of nonaromatic, aromatic, and inorganic sulfur may be detected. This is important for use of CAPTO in selecting those coals which have the greatest upgrade potential when subjected to new or existing sulfur removal technologies.

The improved resolution may also be sufficient for CAPTO to be used as a one step direct determination of organic, inorganic and total sulfur. We are presently completing extensive quantitative studies to assess the feasibility of this determination.

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Table 1
SULFUR DIOXIDE EVOLUTION TEMPERATURES
OF COALS AND MODEL SYSTEMS

COAL/MODEL SYSTEM	TEMPERATURE, DEGREE C AIR, %	TEMPERATURE, DEGREE C AIR, %
Illinois No. 6 (ROM)	330	295
Nonaromatic	470	420
Pyritic	410	450
Sulfate	-	585
Pittsburgh Seam (Ohio No. 8, ROM)	300	300
Nonaromatic	475	420
Pyritic	430	482
Sulfate	-	592
Pyrite (Oxleyer Table concentrated)	620	485
Pyritic	620	580, 595
Sulfate	-	595
Perrone sulfate	620	595
Ferric sulfate	620	595
Polydibenzothioephene	540	450
Polythiophene-tetrahydrothiophene)	300	290
Nonaromatic	475	410
Aromatic	-	-

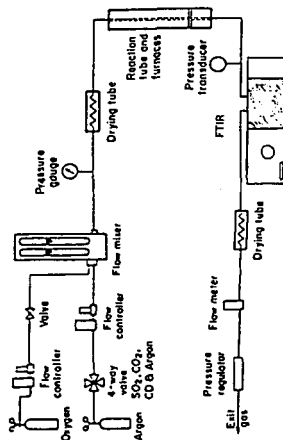


Figure 1. Controlled-atmosphere, programmed-temperature (CAPTO) instrument flow system.

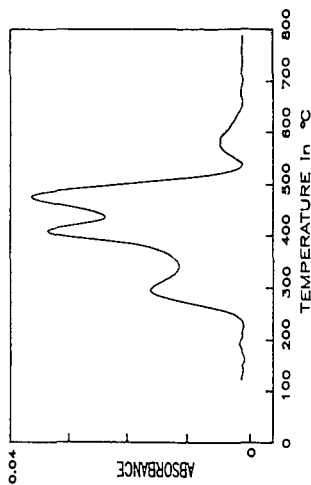


Figure 2. CAPTO evolution profile for sulfur dioxide from Illinois No. 6 ROM coal.

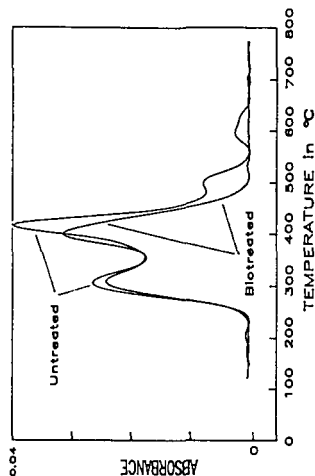


Figure 3. CAPTO evolution profiles for sulfur dioxide from 80 mg of Illinois No. 6 ROM coal (blotreated and untreated).

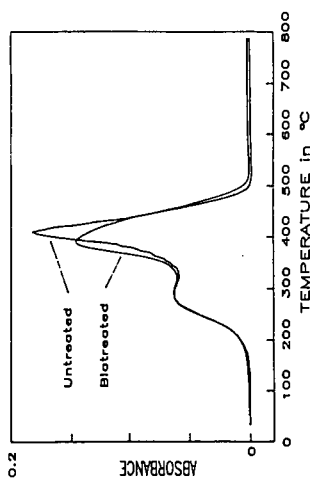


Figure 4. CAPTO evolution profiles for carbon dioxide from 80 mg of Illinois No. 6 ROM coal (biotreated and untreated).

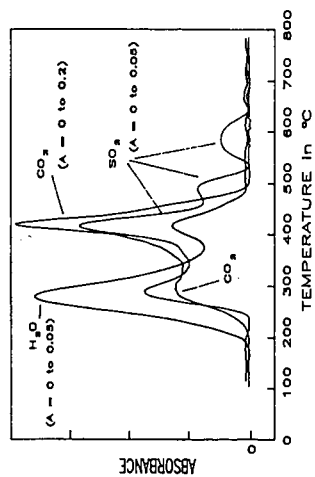


Figure 5. CAPTO evolution profiles from Pittsburgh No. 8 ROM coal (Belmont County, Ohio).

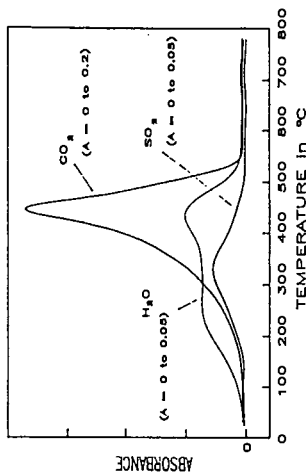


Figure 6. CAPTO evolution profiles from molten caustic treated (438°C) Pittsburgh No. 8 coal.

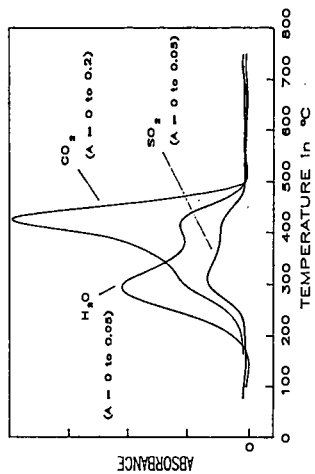


Figure 7. CAPTO evolution profiles from molten caustic treated (415°C) Pittsburgh No. 8 coal.

Transformation Kinetics of Organic Sulfur Forms
in Argonne Premium Coals During Pyrolysis

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The evolution of H_2S during pyrolysis of Argonne premium coal has been monitored with a mass spectrometer in Temperature Programmed Decomposition (TPD) experiments. X-ray Absorption Near Edge Structure Spectroscopy (XANES) and X-ray Photoelectron Spectroscopy (XPS) have been used to follow the changes that occur in the distribution of organic sulfur forms after pyrolysis of these coals to 400°C. The low temperature ($T < 400^\circ C$) elimination of aliphatic sulfur as H_2S is accompanied, in some cases, by the conversion of aliphatic sulfides to aromatic sulfur forms. This work explores the kinetics of H_2S formation. The method of heating rate variation was used in the TPD experiments to derive kinetic parameters for H_2S production during pyrolysis. The results indicate that the decomposition reaction of organic sulfides to form H_2S proceeds prior to most of the conversion of organic hydrocarbons to volatile matter during pyrolysis. This trend is consistent with XANES and XPS findings that there is very little sulfidic sulfur remaining after low temperature pyrolysis of different rank coals.

I. Introduction

Recent advances in the ability to directly quantify sulfur forms in coal by XANES and XPS [1-5] and gaseous sulfur pyrolysis products in a controlled environment [6-8] provides an opportunity to examine the detailed kinetics of the sulfur related chemistry that occurs during laboratory pyrolysis. The monotonic decrease in aliphatic sulfur forms with increasing coal rank has been established by direct measurement [4]. Another XANES and XPS study of several low rank coals has provided evidence that most of conversion of aliphatic sulfides to aromatic forms occurs under milder pyrolysis conditions than those required for the production of almost all of the organic volatile matter of coal [8]. In addition some of the aliphatic sulfur forms are eliminated as H_2S . Pyrolysis studies of model compounds show that organic sulfides are reactive at low temperature ($T < 750^\circ C$) while heterocyclic sulfur structures are not [6,7,9].

The current accuracy of XANES and XPS probes for quantitative determination of organic sulfur forms does not easily allow a detailed kinetic study of the transformation of aliphatic sulfur to aromatic forms during laboratory pyrolysis. While a direct relationship between the initial amount of aliphatic sulfur present in coal and H_2S formed during pyrolysis cannot be made it is certain that the reactions signified by H_2S evolution during pyrolysis of low rank coal are partially responsible for the relatively high levels of aromatic sulfur following mild ($T < 400^\circ C$) pyrolysis [8]. A comparison of the TPD pattern of H_2S evolution for high rank coal with those of very low temperature chars made from low rank coals show that they are remarkably

similar [8]. The present work focuses on the thermal chemistry and the kinetics of the reaction of aliphatic sulfur forms in coals from the Argonne Premium sample program.

II. Experimental

The procedures for obtaining XPS and XANES spectra have been discussed elsewhere [1-4]. XANES experiments were conducted at the National Synchrotron Light Source at Brookhaven National Laboratory on line X-10C. Sulfur speciation was accomplished by spectra reconstruction based on third derivatives of the absorption spectra of model compounds. XPS spectra were obtained on a stand alone laboratory Vacuum Generators (VG) ESCA lab system using 5 channel detection. MgK α non-monochromatic radiation was used. Sulfur speciation was based on a self-consistent curve resolution methodology using experimental instrumental response functions and energy positions from pure model compounds. This methodology has been extensively described [2,4].

The TPD unit is comprised of an ultra high vacuum (UHV) compatible reaction vessel differentially pumped and attached to a UHV main chamber. H₂S detection was accomplished with a mass spectrometer located in the main chamber. The pressure rose to a maximum of 1×10^{-5} torr in the section where the reaction vessel was located and resulted in a maximum pressure rise of 5×10^{-7} torr in the main chamber. A typical coal sample size ranged from 0.5 to 5 mg, loaded into a 3mm x 15mm ceramic vessel. A fine chromel-alumel thermocouple was inserted into the center of the sample bed and the top of the vessel was packed with quartz wool. The vessel was indirectly heated by surrounding tantalum resistive heating elements. Linear heating rates of from 0.05 to 5.0°C/sec were used. Further details of this experimental arrangement appear elsewhere [8,10].

The method of heating rate variation was used to analyze the TPD data [11-13]. A plot of $\ln B/Tp^2$ (vs) $1/Tp$ where B equals the experimental heating rate and Tp equals the temperature of the peak maximum, produces a line with slope equal to $-(E_a/R)$ [11,12]. These Arrhenius parameters provide input for a more detailed discrete distribution of activation energy kinetic model.

The model is based on parallel first order reactions to describe the pyrolysis kinetics of H₂S evolution. The preexponential factor was determined from the experimentally derived activation energy and peak maximum. In order to describe the potential contribution from multiple kinetic processes to the TPD spectrum, a series of kinetic expressions was calculated at 2 kcal/mole increments about the experimentally derived energy value for the peak maximum while the preexponential factor was assumed to remain constant. The temperature of the peak maximum for each process is fixed by these constraints for a given heating rate. The level of contribution from each assumed first order reaction, calculated at 2 kcal/mole increments, is determined by a least squares fit of the calculated sum to the experimental data. Least squares calculations were done using a Cray X-MP/14se computer.

III. Results and Discussion

XANES and XPS were used to characterize the level of aliphatic sulfur initially present in fresh Argonne premium coal samples and following brief pyrolysis of coal at 400°C. Table I shows the results. The change in the relative aliphatic content is most pronounced for lower rank that have high initial aliphatic sulfur

contents. Most of the aliphatic sulfur is converted to aromatic sulfur forms or eliminated as H_2S during this mild pyrolysis. The XANES data for Illinois #6 char produced at 700°C show that there is little further decline in the aliphatic content.

The evolution of H_2S measured by TPD from Argonne Premium coals at a fixed heating rate of 0.23°C/sec is shown in Figure 1. The position of the peak maximum occurs at a lower temperature as the coal rank decreases. The very sharp H_2S evolution spike seen at high temperature in all cases is associated with pyrite decomposition. This sharp spike is not apparent in coals with high organic sulfur and very low inorganic sulfur. As an example of this, the sharp spike is not observed with samples of depyritized Illinois #6 coal nor with samples of extracts of Illinois #6 coal since neither contains pyrite. Lower rank coals such as Wyodak and Illinois #6 show a distinct peak near 400°C in the TPD H_2S trace. For higher rank coals such as Pocahontas the onset of evolution occurs at much higher temperature and appears almost as a shoulder on the sharp pyrite related spike. Coals such as Wyodak and Illinois #6 provide the opportunity for more accurate and detailed analysis.

Ion peaks of evolved gases during TPD experiments at varying heating rates were measured for Illinois #6 and Wyodak coal. The kinetic behavior of gases other than H_2S have been extensively studied [14-16] and their kinetic behavior is important to tie the present work to other kinetic studies. The resultant Arrhenius plot for H_2S , CH_4 and light hydrocarbons ($m/e = 41$; C_3-C_9) determined in this work are shown in Figure 2. The different products show distinct kinetic patterns that will be discussed below. The resultant activation energies derived from the slopes of the lines in Figure 2 appear in Table II along with the calculated preexponential factor. The activation energy is based on least squares analysis. The comparable data for Wyodak coal is also found in Table II.

The position of the $m/e = 41$ peak is closely related to the position of the peak maximum for tar production as measured by infrared at the same heating rate for the Argonne Premium coals [17]. The activation energy and preexponential factor for hydrocarbons from Illinois #6 coal are in good agreement with those of previous studies [15,16]. The kinetic parameters for hydrocarbons from Wyodak coal also agree with previous findings [15] except in one where roughly a 10 kcal/mole higher activation energy was found [16]. The rate constants, however are similar. The present findings appear more reliable since only 3 different heating rates were used in reference [16], while the results of the present work are based on a larger number of experiments.

The kinetic parameters for H_2S evolution from Argonne Premium coals have not been previously examined. Table II shows those for H_2S are significantly different than those for hydrocarbons. The reactions responsible for the elimination of H_2S from Illinois #6 and Wyodak coals happens faster than those that produce most of the volatile hydrocarbons during thermolysis. It is recognized that a single first-order reaction does not provide a good description of the complex hydrocarbon pyrolysis processes of coal [16]. While a single first-order expression is inadequate for a complete description of the H_2S TPD data, most of the H_2S evolution at different heating rates can be accounted for using a small number of Arrhenius for each coal. The TPD data for H_2S were analyzed in the context of the discrete distribution of activation energy kinetic model described in the Experimental section. Table III shows the results of the analysis. Figure 3 shows the TPD spectrum

of H₂S from Wyodak coal at a heating rate of 0.2 deg/sec and the simulated TPD spectrum based on the results of the discrete distribution of activation energy kinetic model. Contributions related to the pyrite H₂S spike are not considered. Table III shows that processes with activation energy lower than the value of the main peak contribute more in the case of Wyodak, a lower rank coal relative to Illinois #6.

It is interesting to note that the present kinetic results can be examined in the context of the early stages of coal metamorphism. Extrapolation of the results for H₂S derived here for Wyodak and Illinois #6 coal, to geological temperatures and times (several million years below 100°C) would predict that much of the H₂S would have been eliminated prior to the loss of much of the other hydrocarbon matter. The relative hydrocarbon kinetic reference is taken as that of the m/e = 41 peak. The H₂S is predicted to be progressively eliminated over extremely long times at low temperature as coal rank increases. The present kinetic data for H₂S along with XANES and XPS data on the depletion in the relative level of aliphatic sulfides still leaves open the possibility that the organic reactions specific to sulfur that occur during laboratory pyrolysis may be related to those that occur during the early stages of coal metamorphism.

IV References

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Table i

Mole percent aromatic Sulfur by XPS and XANES for Argonne Premium Coal Samples Before and After 400°C Pyrolysis

Coal	% Carbon (dmmf basis)	XANES		XPS	
		Fresh	Char	Fresh	Char
Beulah-Zap	74.05	63	94	55	-
Wyodak-Anderson	76.04	67	89	63	84
Illinois #6	80.73	67	95	69	87
Blind Canyon	81.32	76	95	65	-
Pittsburgh #8	84.95	78	95	75	-
Lewiston	85.47	80	91	86	-
Upper Freeport	88.08	87	96	81	-
Pocohontas	91.81	87	94	100	-

Table II

Kinetic Parameters for Pyrolysis Products Determined by the Method of Heating Rate Variation

Coal	Product	Preexponential Log A	Activation Energy kcal/mole	Number of Experimental Observations
Wyodak	H ₂ S	11.8	44.7 (+1.1)	6
Illinois #6	H ₂ S	11.9	45.0 (+2.3)	7
Wyodak	C ₃ -C ₈	13.0	50.8 (+1.2)	17
Illinois #6	C ₃ -C ₈	12.9	50.6 (+1.0)	11
Wyodak	CH ₄	11.8	50.0 (+2.0)	14
Illinois #6	CH ₄	11.8	50.4 (+2.1)	10

Table III

Distribution of Activation Energies Found to Simulate H₂S Evolution. The Contribution of Each Kinetic Process is Calculated Using a 2 kcal/mole Energy Increment. The Amount Due to Processes >+4 and those <-4 kcal/mole Have Been Combined in the Table. All Values Are Listed as the Percentage of the Total.

Coal	<-4	-2	Main Peak	+2	>+4
Wyodak	16	20	26	16	22
Illinois #6	3	13	41	11	32

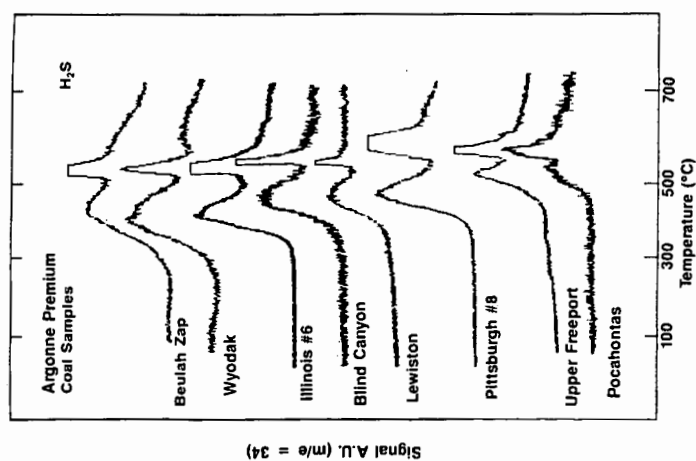


Figure 1

The H₂S TPD Spectra of Argonne Premium Coals.
The Heating Rate Was 0.23 deg/sec.

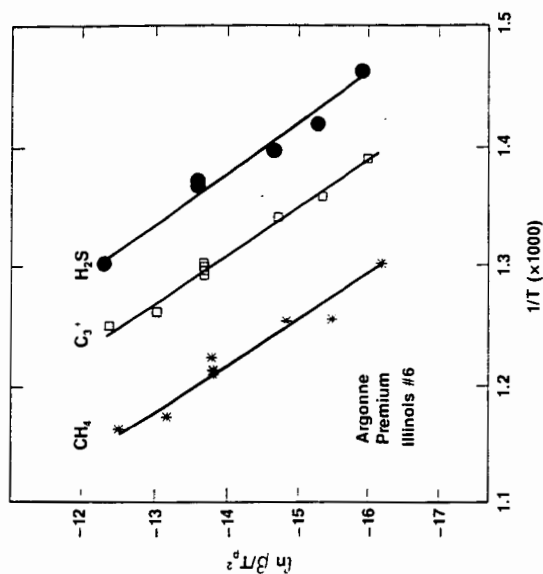


Figure 2

Arrhenius Plot Derived From the Method of Heating
Rate Variation For Argonne Premium Illinois #6 Coal.

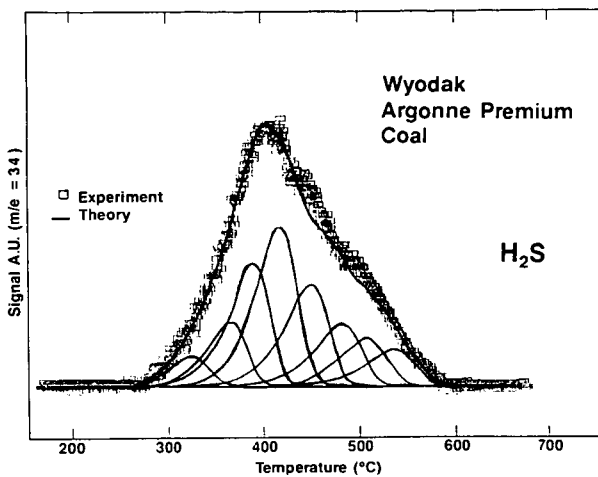


Figure 3

An Example of the H₂S TPD Spectrum of Argonne Premium Wyodak and the Simulated Spectrum Based on the Discrete Distribution of Activation Energy Kinetic Model. The Heating Rate Was 0.23 deg/sec. The Sharp Pyrite Related H₂S Spike Is Not Considered.

DIFFERENTIATION OF PRIMARY, SECONDARY, AND TERTIARY AROMATIC AMINES IN FOSSIL FUELS USING TRIFLUOROACYLATION

I. ANALYTICAL METHODOLOGY

By

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INTRODUCTION

Aromatic amines are of interest to the refiner because they are produced during the conversion of the heavy ends of petroleum to distillate fuels (1,2). Synthetic crudes from coal and shale oil also contain aromatic amines. In coal liquids, primary polyaromatic amines have been implicated as the most mutagenic compound class present (3).

Until recently, aromatic amines were difficult to differentiate in fuels using GC/MS because of the similarity of electron impact fragmentation patterns of underivatized primary, secondary, and tertiary amines. During the late 1960's, an improved analysis of these compounds as trifluoroacetamide derivatives was reported by Saxby et al. (4-6). Since then, several researchers have reported using acetylation and trifluoroacetylation to distinguish between primary and tertiary aromatic amines in gasoline (7), creosote oil (8) and coal liquids (9-12). Later et al. used an analogous derivatization with pentafluoropropionic anhydride to detect primary aromatic amines in an SRC II coal liquid (13,14), and Bartle et al. adducted anilines with hexafluoroacetone for analysis via ^{19}F nuclear magnetic resonance spectroscopy (15).

In these acetylations, one acetyl or trifluoroacetyl group was substituted onto both primary and secondary amines, such as anilines or partially hydrogenated azaarenes. Tertiary aromatic amines, i.e., azaarenes such as naphthenopyridines or quinolines, did not react. The increased mass and easily distinguished fragment ions of the derivatized compounds, as well as shifts in their GC retention times, were used to aid in their identification using GC/MS.

However, monotrifluoroacetylation does not distinguish between primary and secondary amines which are isomass. For example, aminoindans, which are primary amines, will have the same mass (229) as methyl indoline and 1,2,3,4-tetrahydroquinoline after derivatization. The differentiation of primary and secondary amines is important when developing improved processes for the upgrading of heavy ends of petroleum. Research on the hydrodenitrogenation (HDN) of heavy crude feedstocks would benefit from improved analytical techniques which would allow better monitoring of the concentration of aromatic amine intermediates (16).

For these reasons, an analytical method which distinguishes between primary, secondary, and tertiary aromatic amines has been developed. Rigorous reaction conditions are used to form di- and mono-trifluoroacetylated derivatives of primary and secondary amines, respectively. GC/MS is then used to analyze the derivatized base concentrate. The method has been applied to the analysis of a mildly upgraded SRC II coal liquid and preliminary results are reported here.

EXPERIMENTAL

Fuel Fractionation

The history of the raw and hydroprocessed SRC II coal liquid is described elsewhere (17). The feed (HT-9) and a mildly upgraded product (HT-8) were distilled into 200-325° C distillates, acid-base-neutral separations were performed (18), and bases were subfractionated into 7 fractions (19). The whole base fraction accounted for 7.9 percent of feed and 14.1 percent of the hydrotreated (980 SCF/bbl H₂ consumption, 325° C, NiMo catalyst, 1.0 LHSV) 200-325° C distillate (2).

Chemical Derivatization

Standard blends of 6-8 pure compounds, retention index markers (4-fluorophenol, 1-naphthol, and 9-phenanthrol), and an internal standard (4-fluoroaniline) were prepared in dichloromethane (5 mg/mL/component). Concentrations of 50 mg/ml for base fractions, with 5 mg/mL internal standard and retention index markers, were typical. Aliquots (0.2 µl) of the above mixtures were combined with 0.5 mL catalyst (0.8 M 4-dimethylaminopyridine (DMAP) or 4-pyrrolidinopyridine (PPY) in dichloromethane) and 0.4 mL trifluoroacetic anhydride in a 5 mL heavy wall glass reaction vial (Supelco, Bellefonte, PA, cat. 3-3299) fitted with a Teflon cap (ibid., cat. 3-3303). Samples were held at 60° C for 10 minutes, and rapidly cooled. Hexane (2.0 mL) was added, samples were shaken well, and chilled at 0° C to facilitate precipitation of the catalyst as its trifluoroacetate salt. The supernatant was analyzed within 5 hours.

GC/MS

A Kratos (Ramsey, NJ) MS-80 GC/MS system consisting of a Carlo Erba model 4162 temperature programmed GC, modified in-house with a Hewlett-Packard cool-on-column inlet, capillary direct interface, EI source, MS-80 magnetic scan mass spectrometer and Data General Nova 4-based DS-55 data system was used for all analyses. Samples (0.2 to 0.4 µl) were injected, and the column (Restek Corp., Bellefonte, PA, RTX-1 fused silica, 105 m, 0.25 mm I. D., 0.5 µm film) was held 2 minutes at 30° C, programmed at 20° C/min to 70° C, then 2° C/min to 320° C, and held 10 minutes.

Other instrumental conditions were : GC/MS interface 310° C, He column flow 1 mL/min, column head pressure 3.0 Kg/cm²; mass spectral conditions - 70 eV ionizing voltage, 1,000 resolution, 0.5 sec/decade scan rate, source pressure 10⁻⁵ torr, and source temperature 300° C.

Retention Indices

The retention indices were calculated using acetylated 4-fluorophenol, 1-naphthol, and 9-phenanthrol as reference compounds as shown in Eq. 1, below:

$$\text{Eq. 1} \quad I_x = 100 \left[I_N + \frac{t(x) - t(N)}{t(N+1) - t(N)} \right]$$

I_x is the retention index and $t_{(x)}$ is the retention time of each acetylated amine derivative, and $t_{(N)}$ and $t_{(N+1)}$ are the retention times of the acetylated reference compounds whose elution times bracket each amine. I_N for 1-fluorophenol is 1, 1-naphthol is 2, and 9-phenanthrol is 3, with N representing the number of aromatic rings present in each reference compound.

Although it is customary to use retention index reference compounds with the same functionality as the compounds examined, phenols were used here for two reasons. First, these same reference compounds were used to calculate a large body of retention indices reported earlier for trifluoroacetylated hydroxyaromatics (20). Use of the same reference compounds will allow a common basis of comparison of trifluoroacetylated fuel components. Secondly, 2- and 3-ring trifluoroacetylated hydroxyaromatics are stable at GC temperatures which cause breakdown of the equivalent 2- and 3-ring diamides. If desired, the $I_{(x)}$ values reported here can be converted to values based on aromatic amines as reference compounds.

Relative Response Factors

Relative response factors (RRF) were calculated according to Eq. 2, below:

$$\text{Eq. 2} \quad \text{RRF} = (A_x/A_s)(W_s/W_x)$$

where A = area percent, based on the GC/MS total ion current, and W = weight, x = derivatized aromatic amine, and s = derivatized standard (4-fluoroaniline).

RESULTS AND DISCUSSION

Derivatization Reactions

Table I lists the compounds derivatized to form amides along with their retention indices (I_x) and their total ion current responses relative to that of 4-fluoroaniline (RRF). The compounds are listed in their underivatized form, grouped into primary, secondary, and tertiary amines.

In general, primary aromatic amines such as anilines and aminoindans are reacted twice to form di-trifluoroacetamides (diamides), secondary amines such as N-alkylanilines, 1,2,3,4-tetrahydroquinolines, indolines, and carbazoles, react once to form monotrifluoroacetamides (mono-amides), and tertiary amines such as quinolines and 2,3-cyclohexenopyridines (5,6,7,8-tetrahydroquinolines) do not react.

A catalyst is necessary during the reaction (21, 22). Initially, DMAP was used as a catalyst, but PPY was found to provide more complete trifluoroacetylation of some compounds. Reaction conditions were optimized using 2,6-diethylaniline, which is a sterically hindered primary amine, and N,N-diethylaniline, which is a tertiary amine that undergoes ring acetylation at the ortho and para positions. Catalyst and reagent concentrations and reaction time (10 minutes) were held constant and the reaction temperature was varied. At room temperature, 58 percent of the 2,6-diethylaniline was converted to the diamide derivative, with the balance in the monoamide form. At both 50 and 60° C, it was 100 percent converted to the diamide form.

It was initially hoped to avoid ring acetylation of N,N-dialkylanilines using mild reaction conditions, but, at room temperature, N,N-diethylaniline was completely converted to the mono-ring-acetylated form, with 92 percent addition at the para- and 8 percent at the ortho-position. No evidence for the addition of more than one trifluoroacetyl group to the ring was found at either 50 or 60° C when the supernatant was analyzed within 4 hours storage at 0° C. The appearance of

"over-reaction" peaks was noted after 6 hours storage, however, so subsequent samples were analyzed within 5 hours of derivatization and storage.

One other tertiary amine, 2,3-cyclopentenopyridine, underwent ring-acetylation, forming a derivative with mass 311, indicating addition of 2 trifluoroacetyl groups to the saturated ring. The percentage of the derivative formed was quite reproducible, however, as shown by a RRF standard deviation of 6 percent. 2,3-cyclohexenopyridine (5,6,7,8-tetrahydroquinoline) and its alkyl-substituted homologs did not form derivatives.

The percentage of each aromatic amine which reacted to form the expected derivative is shown in Table 1, column 3. Twenty five of the 31 primary aromatic amines formed only diamides. Those cases of incomplete conversion were generally of two types. The first includes compounds such as methylbenzylamines, where the relatively low acidity of the amine hydrogens makes their displacement difficult. The second type involves higher boiling aromatic diamides, which appear to thermally decompose above a column elution temperature of about 200° C.

Derivatization Reproducibility

Each blend of aromatic amines and internal standards was derivatized 3 times, and each reaction mixture was analyzed twice, with no more than 5 hours between GC/MS injections. As shown in Table 1, replicate response factors from the 6 runs on each blend typically varied less than ± 10 percent. Since this variation included contributions from both GC injections and mass spectral measurements, the reproducibility of replicate reactions was undoubtedly higher than 90 percent in most cases.

The few examples where RRF standard deviations varied more than ± 10 percent were caused either by derivative decomposition on-column or by the tailing of underivatized tertiary amines such as quinoline (± 24.7 percent) or N,N-dimethylbenzylamine (± 27.7 percent) on the capillary column.

Mass Spectral Fragmentation Patterns

Trifluoroacetyl derivatives of primary aromatic amines typically show strong molecular ions and distinctive mass fragmentation patterns. Characteristic $[M-69]^+$ and $[M-97]^+$ ions are present in mass spectra of almost all aromatic amine derivatives, but the $[M-97]^+$ ion is usually more prominent for amide derivatives, and $[M-69]^+$ more intense for carbon-acylated compounds. Spectra of 2-n-alkylanilines usually show a fragment at $[M-18]^+$, corresponding to loss of H_2O . The major fragment in 4-n-alkylaniline derivatives corresponds to benzylic cleavage of the n-alkyl group. Addition of the trifluoroacetyl group(s) often markedly changes the fragmentation pathway of the derivative compared to the parent compound (21).

Figure 1 shows the spectra of 4 underivatized isomeric aromatic amine compounds of interest in HDN studies; 2,3-cyclohexenopyridine (a), 1,2,3,4-tetrahydroquinoline (b), 1,2,3,4-tetrahydroisoquinoline (c) and 5-aminoindan (d). Three of the spectra (a, b, and d) are virtually indistinguishable, and the fourth (c) differs only by the presence of a prominent m/z 104 fragment. Derivatization, however, enables differentiation of all four compounds, since, as shown in Figure 2, (a) remains unchanged, while (b) and (c) form mono- and (d) diamides. The two monoamides can be easily differentiated by a fragment at $[M-15]^+$, present in the spectrum of (c), but absent in (b). The spectrum of the diamide (d) now shows a molecular ion at m/z 325, 96 mass units higher than that of (b) and (c), and 192 units higher than (a). These spectra illustrate the marked improvement in ease of compound identification after trifluoroacetylation.

SRC II Coal Liquid

SRC II Coal Liquid

The main aromatic amine compound types identified so far in SRC II 200-325° C base fractions are shown in Figure 3. For the hydrotreated fractions, these include: Fraction 4- anilines and 1,2,3,4-tetrahydroquinolines; Fraction 5 - the bulk of the anilines, from C1 through C6, and 4-aminoindan and its alkyl homologs; Fraction 6 - homologues of quinoline and 2,3-cyclohexenopyridines, 5-aminoindan, indoline, an unidentified naphthoquinoline type, and small amounts of alkylanilines, and Fraction 7 - *l*-decahydroquinoline and its alkylhomologues.

Fraction 6 from the feed material (about 70 percent of the total basic nitrogen in the distillate, by weight) consists primarily of azaarenes, with large amounts of quinolines, and some partially hydrogenated nitrogen compounds also present.

The following tentative conclusions may be drawn from data collected so far: First, more decahydroquinolines than 1,2,3,4-tetrahydroquinolines (by weight) are present in the hydrotreated material, as predicted by Steele, et al. (16). Secondly, there are more 2-substituted anilines, particularly 2-ethyl and 2-propyl-, than other isomers, an indication of their production from ring-opening of larger compounds. In general, hydrogenation of the nitrogen-containing aromatic rings in azaarenes occurs preferentially over that of other rings. Compounds such as aminoindans may be derived from partially hydrotreated azaarenes, such as 1,2,3,4-tetrahydroquinolines, via rearrangement, or via some other source.

CONCLUSIONS

Most primary, secondary, and tertiary aromatic amines in fuels boiling below 350° C may be differentiated by the formation of trifluoroacetyl derivatives, which are eluted and identified using GC/MS. Replicate response factors of the derivatives, based on the GC/MS total ion current, typically vary less than ± 10 percent.

ACKNOWLEDGMENT

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TABLE 1

GC Retention Indices and MS Response Factors of Trifluoroacetylated Amine Compounds

CHEMICAL NAME	% Reacted	I _x	Response RRF %G	CHEMICAL NAME	% Reacted	I _x	Response RRF %G
PRIMARY AROMATIC AMINES ¹				SECONDARY AROMATIC AMINES ²			
4-fluoroaniline	100	125.65	1.00	t-decahydroquinoline	100	214.42	1.15
aniline	100	130.16	1.29	N-ethylamine	100	171.90	0.96
2-methylamine	100	142.16	1.16	N-butylamine	100	207.53	1.03
3-methylamine	100	146.64	1.15	1,2,3,4-tetrahydroquinoline	100	219.70	0.97
4-methylamine	100	150.59	1.05	1,2,3,4-tetrahydroisoquinoline	100	227.96	0.93
2,6-dimethylamine	100	156.32	1.10	indoline	100	210.31	0.80
2-ethylamine	100	158.18	1.03	diphenylamine	100	254.43	1.01
2,5-dimethylamine	100	158.46	1.03	N-phenyl-1-naphthylamine ⁴	60	329.78	0.64
3,5-dimethylamine	100	162.66	1.04				5.5
2,4-dimethylamine	100	162.78	1.14	TERTIARY AROMATIC AMINES ³			
2-isopropylamine	100	165.44	1.01	N,N-dimethylamine, para derivative	90	229.71	0.80
2,3-dimethylamine	100	165.51	1.06	N,N-diethylamine, para derivative	96	255.67	1.01
4-ethylamine	100	168.24	1.05	N,N-dimethylbenzylamine	0	147.77	0.59
3,4-dimethylamine	100	172.33	1.00	2,3-cyclohexenopyridine	0	178.42	0.53
2-propylamine	100	173.48	0.92	quinoline	0	180.89	0.73
2,4,6-trimethylamine	100	176.29	1.07	2,3-cyclopentenopyridine	100	212.67	0.81
2,4,5-trimethylamine	100	183.29	1.01				6.5
4-propylamine	100	185.61	1.08				
2,6-diisopropylamine	100	201.02	0.98				
4-n-butylamine	100	204.48	0.83				
4-nonylamine, monoamide	92	317.08	1.19				
4-nonylamine ⁵	8	290.53	0.10				
4-decylamine	31	305.75	0.47				
benzylamine	100	152.73	0.99				
4-methylbenzylamine	92	172.84	0.99				
2-methylbenzylamine	95	173.09	1.12				
(2-aminoethyl)benzene	93	173.26	1.15				
5-aminoindan	100	202.02	0.89				
1-amino-5,6,7,8-tetrahydronaphtha	100	213.38	0.95				
2-amino-5,6,7,8-tetrahydronaphtha	42	258.22	0.49				
2-amino-5,6,7,8-tetrahydronaphtha	36	225.83	-				
2-amino-5,6,7,8-tetrahydronaphtha	100	340.21	1.22				
2-amino-5,6,7,8-tetrahydronaphtha	100	340.21	1.22				
2-amino-5,6,7,8-tetrahydronaphtha	100	233.33	1.03				

4 RRF average of 4 determinations

5 RRF average of 5 determinations

1 di-(trifluoroacetamides), except as noted

2 mono-(trifluoroacetamides), except as noted

3 derivitized compounds are all ring-acylated

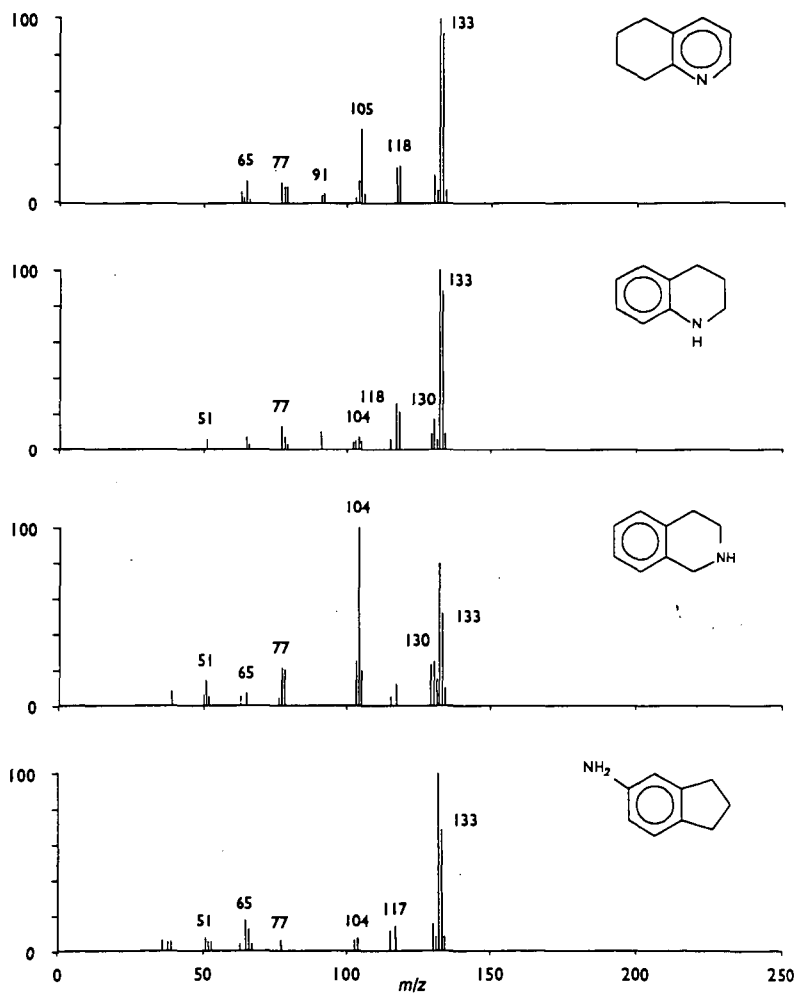


Figure 1. Mass Spectra of Hydrodenitrogenation Intermediates.
(Twenty Most Prominent Ions)

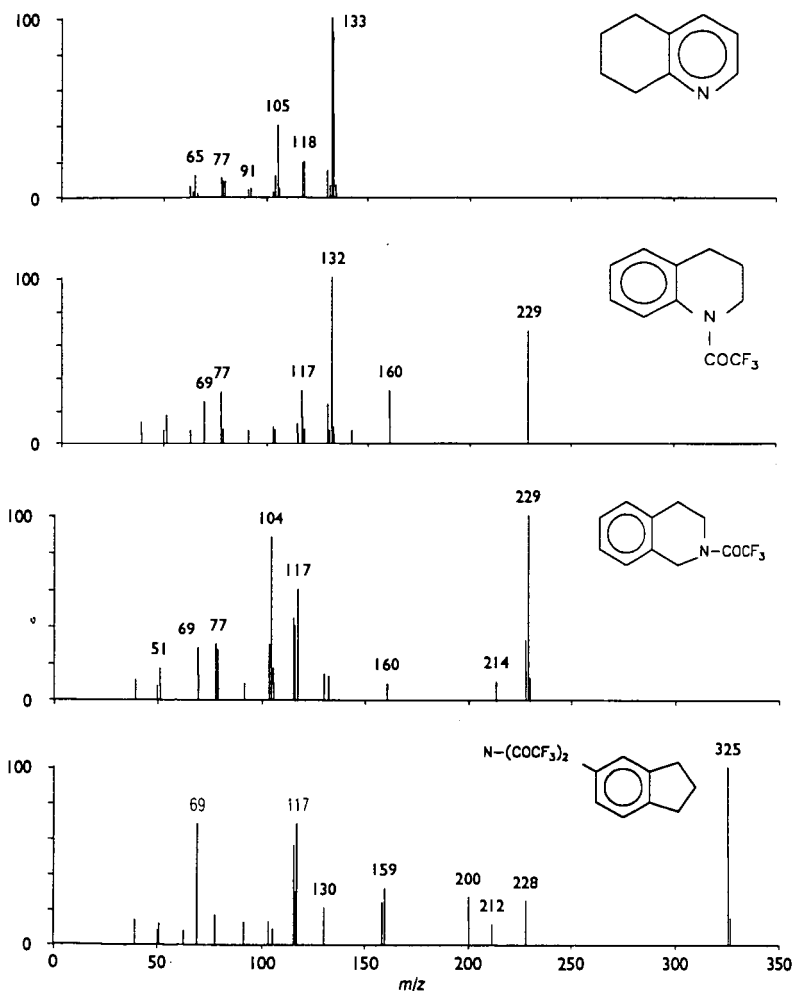


Figure 2. Mass Spectra of Hydrodenitrogenation Intermediates Derivatized to form Mono- or Di-trifluoroacetamides.
(Twenty Most Prominent Ions)

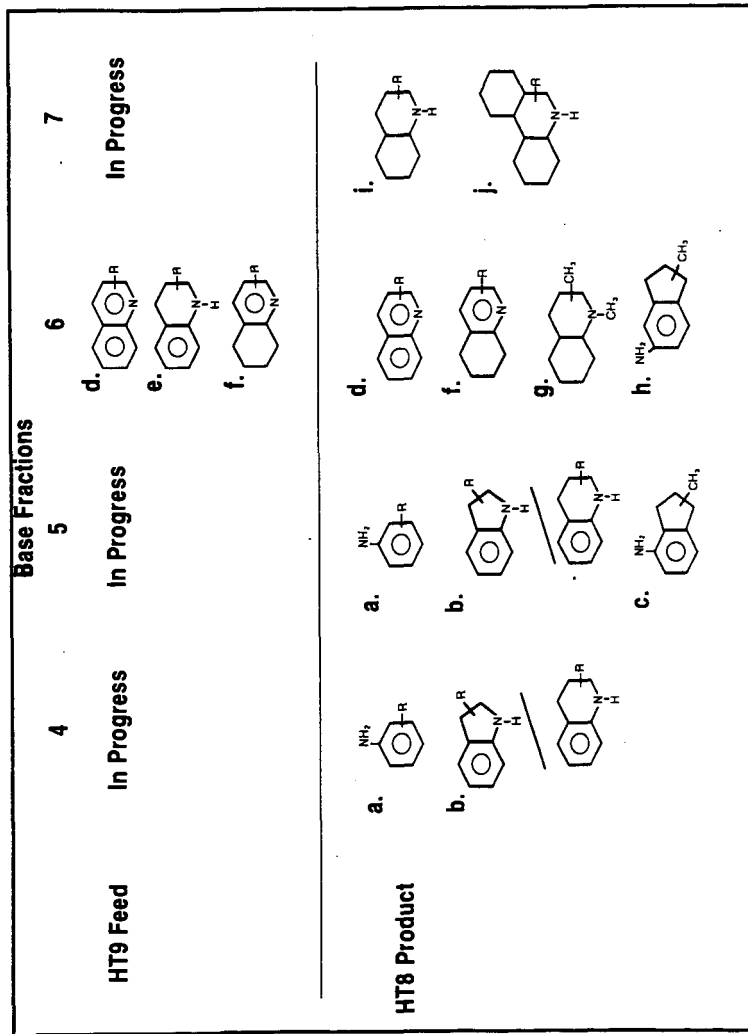


Figure 3. Aromatic Amine Compound Types in an SRC II 200-325° C Coal Liquid Feed (HT9) and Lightly Hydrotreated Product (HT8): a. anilines, b. indolines/1,2,3,4-tetrahydroquinolines, c. 4-aminindans, d. quinolines, e. 1,2,3,4-tetrahydroquinolines, f. 2,3-cyclohexenopyridines, g. N-alkyldecahydroquinoline, h. 5-aminindans, i. decahydroquinolines, and j. tetradecahydrophenanthridines.

PYROLYSIS-FOURIER TRANSFORM INFRARED SPECTROMETRY AS A TECHNIQUE FOR ANALYZING FUNCTIONAL GROUPS WITH OXYGEN IN COAL

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INTRODUCTION

Pyrolysis, flash pyrolysis and thermogravimetric analysis (TGA) were used to characterize coals based on thermolysis products¹⁻⁷. The coals are known to release volatiles such as CO₂ and methane even at sample storage and handling conditions used for Premium Coal samples at Argonne National Laboratory^{9,10}. Coal conversion process produces these volatiles in larger quantities. The maximum amount of small species including CO₂ and CO are produced under pyrolytic and gasification conditions. There are reports on the temperature dependence of the thermolysis of functional groups in coal^{2,4,5}. The volatiles were quite often identified by using techniques such as GC, MS, GC-MS and FT-IR. Long hydrocarbon chains in Texas lignites and other coals were analyzed by Pyrolysis -GC¹. Flash pyrolysis using GC-MS was used for determining organic sulfur structures in coal³. The use of TGA-FT-IR for coal analysis based on devolatilization products has been reported⁶.

Quantification of oxygen in coal is often accomplished by indirect methods. Since the estimation of organic oxygen is interfered by the moisture content and the oxygen in the mineral matter, oxygen content of coal is reported in more than one format⁹. Pyrolysis can convert organic oxygen to oxides of carbon which can be estimated using a gas chromatographic detector. A gas chromatograph with detector for organic oxygen is now available from Carlo Erba for estimating oxygenated organic species. The GC effluents are pyrolyzed at 1400°C. The oxides of carbon are converted to methane with hydrogen in the presence of a Ni catalyst, and the methane is then estimated by flame ionization detector. This technique however cannot distinguish CO₂, CO or CH₄, but the concept that pyrolysis converts organic oxygen to oxides of carbon is established.

Using a continuous-mode pyrolyzing inlet for GC, available commercially⁸, we have conducted experiments to develop a new technique for analyzing coal, particularly the organic oxygen. The samples are pyrolyzed in a pyrolyzer which is fitted to the injection port of capillary gas chromatograph on-line with FT-IR spectrometer with GC-FT-IR interface. The system allows both qualitative and quantitative analyses. The IR peaks of volatiles are at least a hundred fold larger than what is observed by TGA-FT-IR experiments⁶. Small species such as CO, H₂O and CH₄ often missed by GC-MS are easily identified and even estimated by GC-FT-IR. The results of our preliminary experiments using pyrolysis-GC-FT-IR indicate that useful data on organic oxygen as well as its distribution in various functional groups can be obtained.

EXPERIMENTAL

The pyrolysis experiments were conducted using a number of simple organic compounds which were obtained from commercial sources and contained one or more functional groups with oxygen. Eight Premium Coal samples from Argonne National Laboratory were the coal samples. Table 1 lists some of the reported analysis data of the Premium coal samples⁹. The Texas lignite sample was obtained from a local mine at Carlos about twenty miles away from the campus and was analyzed in the Chemistry Department.

The Instrumental setup consisted of a Pyrojector⁸ (Scientific Glass Engineering, SGE, Austin Texas), Fourier Transform infra red (FT-IR) spectrometer (Nicolet 60SXR) with gas chromatographic interface and a capillary gas chromatograph (Hewlett Packard , HP5890) with on-column injection port. The Pyrojector was installed on the on-column injection port using an adaptor made in the machine shop of the Chemical Engineering Department .

Septum injection technique was used. Helium was used as the carrier gas. There were purges at the septum of the pyrojector as well as at the on-column injector. The carrier gas flow through the capillary column was derived from the gas flow through the Pyrojector as well as the carrier gas flow of the gas chromatograph through the injection port. The sample size as well as these flow rates were optimized for quantitative results. The furnace temperature of the pyrojector was varied from 300°C to 1000°C. The GC oven temperature of the gas chromatograph was maintained at 50°C. The FT-IR was used as the detection technique. The gas chromatograph was equipped with a 25 meter 0.32 mm id capillary column with 1 μ m BP-5 (5%phenyl 95% methyl silicon bonded phase, SGE). In this study only smaller species which were volatile in oven at 50°C were detected by FT-IR. A mercury cadmium telluride (MCT-A, Nicolet) detector was used on the gas chromatographic port of the system. The IR spectra were scanned at 4 cm^{-1} resolution. Either 8 or 32 scans were collected per file. The data collection was initiated 1.5 minutes after sample injection and discontinued after 6 minutes. The spectra were collected in this time frame in several files. The spectrum collected just before the appearance of the products was used as background which was subtracted from each sample spectrum.

The instrument was calibrated by injecting 0.25 ml standard gas mixture (2% methane, 20% carbon monoxide, 50% carbon dioxide and 28% nitrogen) using a pressure tight gas syringe. Areas under major IR peaks were used for response factor calculations. Liquid samples were injected using a 10 μ l syringe. The initial Pyrolysis experiments were conducted on acetic acid , ethylacetate, tetrahydrofuran, hydroxybenzoic acid and several other compounds. These compounds represent organic molecules having functional groups with oxygen. Samples were pyrolyzed at temperatures ranging from 400°C to 1000°C in order to determine the optimum temperature for removal of oxygen from these molecules as oxides of carbon. The solid samples were introduced into the Pyrojector either as a pellet (which was prepared using a pelletizer from SGE) or as pressed powder using a solid injector. The sample sizes were 1 mg for pure organic compounds. About 2 mg samples were used for coals. The sample size was not very precise as the powder was packed into the barrel of the solid injector (mostly same volume of powder) and pushed into the inlet of the Pyrojector.

Experiments were also conducted using cryofocussing technique. During the first five minutes after sample injection the volatiles were trapped by cooling a small segment of the capillary column in liquid nitrogen. After five minutes the column was removed from liquid nitrogen and allowed to warm up while scanning the IR spectrum.

RESULTS AND DISCUSSIONS

Making the pyrolysis experiments reproducible was very challenging. Several initial experiments were irreproducible due to leaks and noncompatible flow conditions. The pyrojector was composed of quartz pyrolyzing tube which was heated in a furnace with free standing control module. The samples were injected from the top of the tube through the septum and the pyrolyzed products were immediately swept into the capillary column and to the light pipe of the GC-FT-IR interface. The carrier gas He entered from the top of the pyrojector as well as through the inlet of GC. The gas head pressures at these points were optimized for better detection. This was achieved by varying the head pressures while injecting acetic acid samples. 10 psi He pressure at the Pyrojector head was found suitable while the pressure at the column inlet was kept slightly lower. Both the septum purge of the Pyrojector and GC inlet purge were kept at a level of less than 1 ml per minute. Higher purge flows caused the escape of products. The experiments to calibrate the instrument using standard gas mixture revealed that the gas sample was spread over a 3 minute peak width due to the spreading of the sample in the quartz liner in the Pyrojector. The relative IR response of $\text{CH}_4 : \text{CO}_2 : \text{CO}$ was observed as 4 : 5: 1.

The reports on pyrolysis-FT-IR are limited. In a number of reported studies on the use of TGA-FT-IR, the volatile from the thermographic balance was allowed to pass through a gas cell while scanning FT-IR spectrum. The FT-IR signal intensity was very weak. We are able to obtain very strong signals due to the use of the light pipe in the GC-FT-IR interface instead of a gas cell. The pyrolysis products appear 2 minutes after the injection of the sample and product peaks maximized in 2.5 minutes and was spreading another 2 or 3 minutes. The reason for such tailing was the larger diameter of quartz tubing (volume = 0.5 ml) compare to the capillary column. The experiments using cryofocussing showed the elution of pyrolysis products in narrow bands comparable to capillary GC peaks. When cryofocussing was used, the products had undergone gas chromatographic separations. Both CO and methane appeared first, and CO_2 eluted later. For the comparative study of coals the spectrum collected at 2.5 minutes without the aid of cryofocussing was used as it included all the light products.

The thermal decomposition of simple organic compounds depends on the nature of functional group as well as on the pyrolytic temperature. The effect of pyrolysis temperature on acetic acid is shown in Figure 1. At temperatures below 650°C acetic acid pyrolyzed to produce small amounts of CO_2 . Methane and CO were produced at 750°C and above. At 750°C tetrahydrofuran (THF, Figure 2) did not produce any oxides of carbon. However at 800°C it pyrolyzed to produce CO and hydrocarbons including methane. No CO_2 was produced from THF indicating that the oxygen from ether link can only be extracted as CO but requires higher temperatures. The amount of CO produced from THF did not increase at higher temperatures. If all the ethers behave like THF the oxygen from ethers can be extracted as CO at 800°C . Ethylacetate (Figure

3) produced CO_2 and relatively higher levels of CO compared to acetic acid. The CO production peaked at 800°C for both acetic acid and ethyl acetate and levels went down at higher temperatures. At 950°C methane and other hydrocarbons were produced the most. Methanol thermolyzed to CO, CO_2 and H_2O below 800°C and CO was the predominant species above 950°C. Ethanol produced only CO at 800°C and above.

Hydroxy benzoic acid has two functional groups -- hydroxy group and carboxylic group. Based on the results from the experiments with alcohols such as methanol and ethanol the hydroxyl group was expected to produce CO at temperatures above 800°C. Figure 4 shows that both CO_2 and H_2O were produced at lower temperatures. The oxygen in hydroxyl groups can be extracted either as water or as CO. At temperatures below 800°C only H_2O was formed. CO was formed most at 950°C.

The FT-IR spectra of volatiles from Texas lignite pyrolyzed at different temperatures is shown in Figure 5. The CO_2 and CO obtained at 700°C was from the carboxylic groups. Since the amount of CO does not increase from 700 to 800°C the ether bond represents only a small fraction of organic oxygen in lignite. The amount of CO produced at 1000°C is 50% higher than at 800°C, about 1/3 of all the CO was from hydroxyl groups. Of the oxygen extracted as oxides of carbon by pyrolysis at 1000°C, about 90% of the Oxygen was in the carboxylic groups and 10% was from the hydroxyl groups and less than 1% could be from ether groups

Premium Coal samples were also subjected to pyrolysis at temperatures from 400°C to 1000°C. Injection of packed powdered sample was easy at 700°C and above. Lower temperatures produced mostly CO_2 . Experiments conducted at 750°C produced CO_2 , CO and CH_4 and is used for illustration. Table 1 lists all the coals and its oxygen content on an ash free basis and the products evolved. The FT-IR spectrum of the thermolysis products are shown in Figure 6. There is direct relationship between the oxygen content and CO_2 and CO produced. Higher temperatures produced slightly more oxides of carbon but did not observe any enhancement of CO.

CONCLUSIONS

Preliminary studies on Pyrolysis -GC-FT-IR of pure organic coals indicates that the analytical techniques can be developed for identifying and estimating oxygenated functional groups in organic species. The order at which functional groups thermolyzed is follows:- Carboxylic groups at 700- 800°C, ether groups at 800-900°C and hydroxy groups 900-1000°C or higher temperatures. The preliminary test results strongly supports the viability of the technique.

ACKNOWLEDGEMENTS

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Table 1 Analysis⁹ and pyrolysis data of the coal samples

	Ash	Volatile	Oxygen	CO ₂	CO
Texas Lignite	23.6	39.5	26	0.33	0.12
Wyodak Subbitumino	6.3	32.2	18	0.15	0.05
ND Beulah-Zap	6.6	30.5	20.3	0.14	0.04
Illinois #6	14.3	36.86	13.5	0.09	0.06
Blind Canyon Seam	4.5	43.7	11.6	0.05	0.03
Pittsburgh #8	9.1	37.2	8.8	0.03	0.02
Penn Upper Free Port	13	27.1	7.5	0.02	0.04
Stockton Seam	19.4	29.4	9.8	0.02	0.01
Pocahontas #3	4.7	18.5	2.5	0.01	0.01

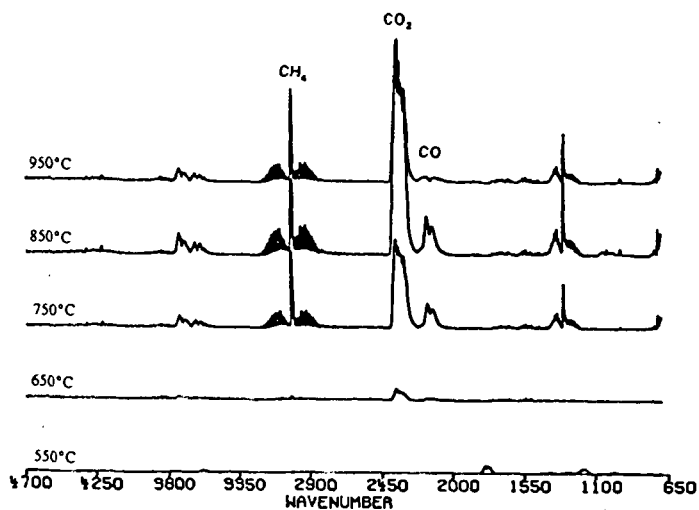


Figure 1. FT-IR spectra of decomposition products of acetic acid as a function of Pyrojector temperature.

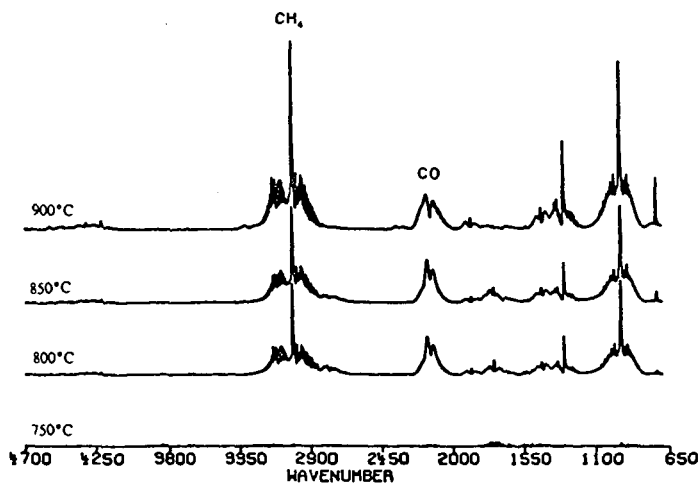


Figure 2. FT-IR spectra of decomposition products of tetrahydrofuran(THF) as a function of Pyrojector temperature.

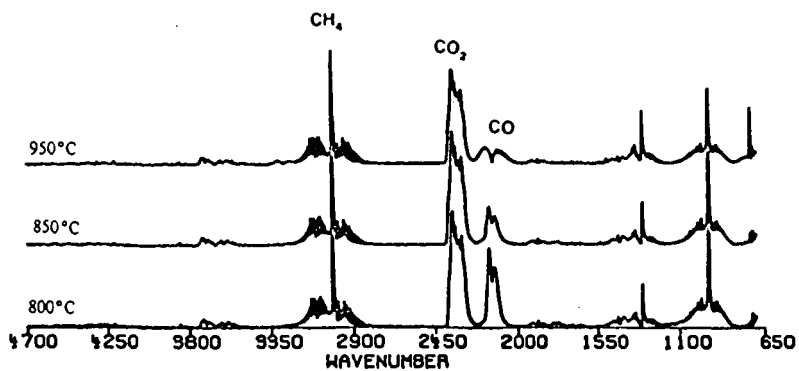


Figure 3. FT-IR spectra of decomposition products of ethyl acetate as a function of Pyrojector temperature.

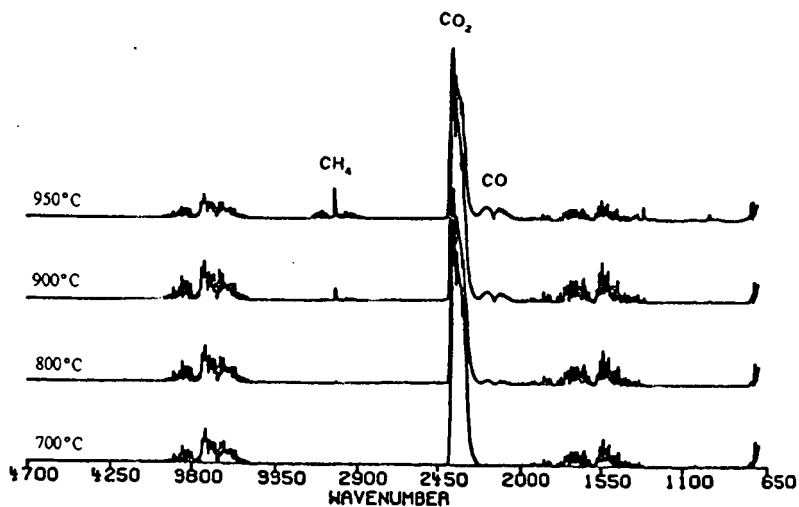


Figure 4. FT-IR spectra of decomposition products of hydroxy benzoic acid as a function of Pyrojector temperature.

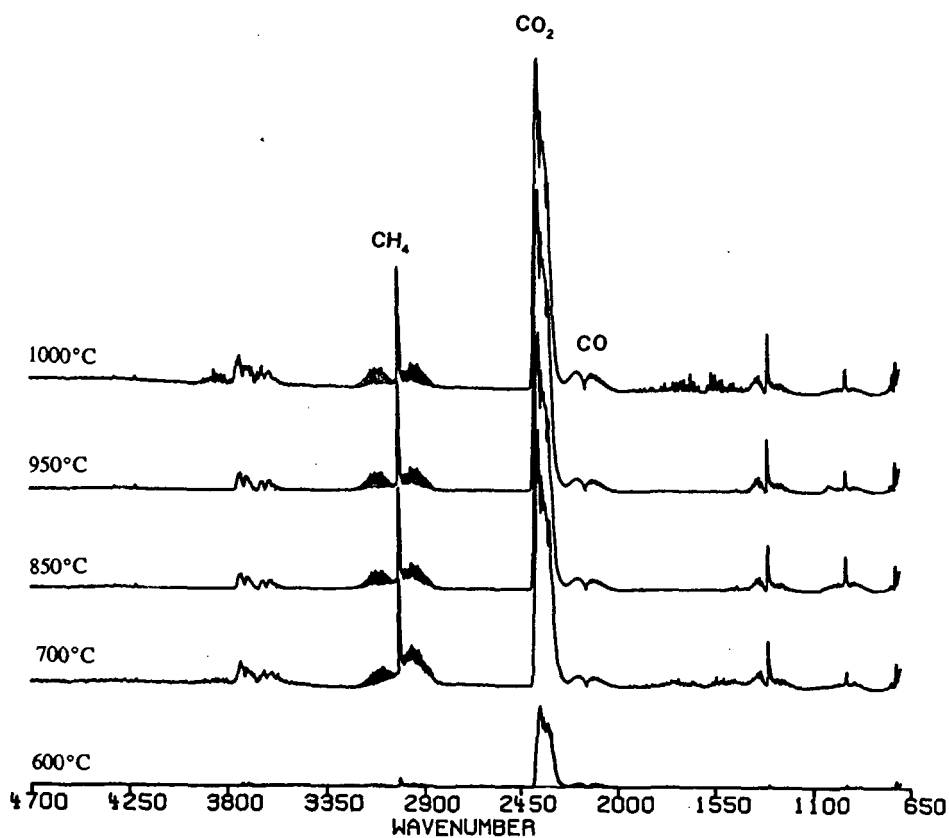


Figure 5. FT-IR spectra of decomposition products of Texas lignite as a function of Pyrojector temperature.

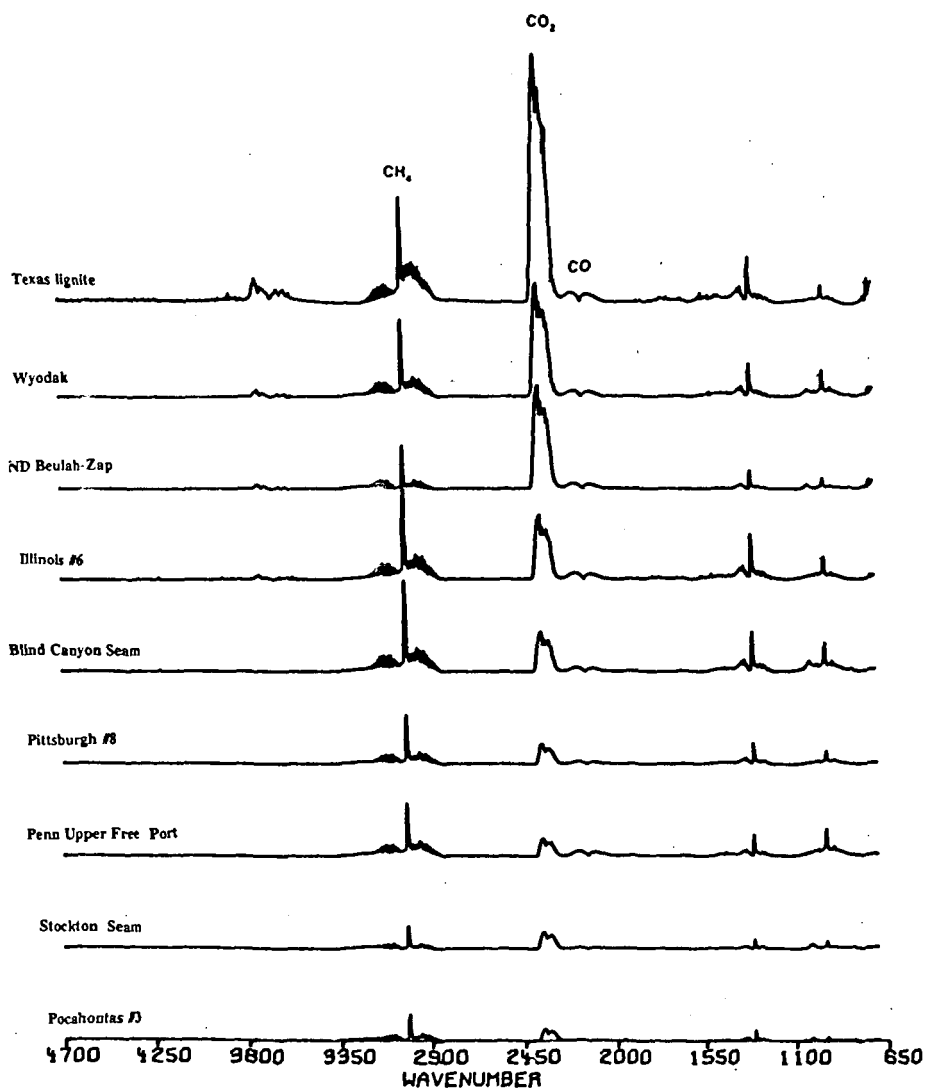


Figure 6 FT-IR spectra of pyrolysis products obtained from Texas lignite and Premium Coals. Pyrolysis temperature, 750°C

CHARACTERIZATION OF THE ARGONNE PREMIUM COAL SAMPLES BY FIELD IONIZATION MASS SPECTROMETRY

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Keywords: FIMS, Argonne Premium Coals, Pyrolysis

INTRODUCTION

The technique of field ionization mass spectrometry (FIMS) has proven to be quite useful for analyzing complex mixtures, particularly fossil fuels. (1) The technique of field ionization (FI) consists of ionizing molecules by the application of an intense electric field and results in the formation of only the molecular ions for most organic compounds. (2) Thus, complications arising from fragmentation during ionization are minimized in this method. Another advantage of field ionization is that the relative field ionization efficiencies of various hydrocarbon types are within a factor of two of alkyl aromatics except for saturated acyclic hydrocarbons, which ionize about a third as efficiently. For many other ionization techniques such as field desorption or low-voltage electron impact, the relative ionization efficiencies can differ by as much as two orders of magnitude. Thus, even without any corrections for sensitivity, the FI mass spectra represent the true molecular weight profile fairly accurately.

In this paper we present the results obtained by pyrolyzing the eight coal samples from the Argonne Premium Coal Sample Program (APCSP) in the inlet of the mass spectrometer and analyzing the volatiles by FIMS. From these data we can deduce relative amounts of several structural types. We also identify salient rank-dependent trends. Some of these trends are known from other studies, (3-6) but FIMS provides an easy means for quantifying them and developing indices that could be used in modeling.

EXPERIMENTAL

The FIMS system used in this study has been described elsewhere. (7) It consists of an activated tantalum foil field ionizer interfaced with a 60° magnetic sector mass analyzer and a PDP 11/23 computer for data acquisition and processing. In a recent study of various configurations for mass spectrometric analysis of coals, Muezelaar and coworkers reported that a combination of direct insertion pyrolysis followed by FI and magnetic sector mass analysis provides the most detailed and accurate mass spectra. (4) We find this result gratifying because it basically vindicates our approach. Approximately 1-2 mg of the sample is introduced via a heatable direct insertion probe. Mass spectral data of the evolving tars are collected by repeatedly scanning the magnet over a preset range (50 to 1400 Da) while the sample is gradually heated at a fixed rate of 5°C/min from the ambient temperature to approximately 700°C. At the end of the run, the sample holder is retrieved and weighed to determine the fraction that was devolatilized during the analysis. For a given sample, many spectra are collected, each representing a certain range of temperature. The individual spectra are added and normalized to obtain a spectrum of the evolved tars. These spectra are also used to produce a thermal evolution profiles of the total tars or of selected mass peaks.

RESULTS AND DISCUSSION

Mass Spectral Profiles

The spectra for the total tars evolved during temperature-programmed pyrolysis for the Argonne coals are shown in Figures 1 and 2 in the order of increasing rank. Several features are immediately apparent and noteworthy. In general, the spectra appear to be composed of two groups of peaks: (a) there is a cluster of peaks consisting of various homologous series in the low molecular weight range (100-200 Da) and (b) a broad, roughly gaussian, distribution of peaks spanning the mass range of 150 to 1000 Da. The low molecular weight cluster is particularly dominant in the Beulah Zap lignite and the Wyodak subbituminous coal. With increasing rank, the prominence of this cluster decreases relative to the broad gaussian

envelope, whose mean appears to shift to higher masses with increasing rank. In the higher rank coals there is also a second cluster of homologous peaks in the 200 to 400 Da range riding on the broad profile. A few peaks in the 300 to 350 Da range that are substantially more intense than the general profile can be seen in the spectrum of the the Utah coal. These peaks are most likely due to biomarkers. The most intense among these is at 324 Da, which corresponds to a tetracyclic monoaromatic alkane ($C_{34}H_{36}$). There is also a peak at 320 Da, which would correspond to the diaromatic analogue. Interestingly, these peaks have also been observed in the terpenoid resins associated with other coals from Utah.(8)

Chemical Characterization

The most prominent peaks in the low molecular weight range are at m/z 84, 108, 110, 122, 124. These peaks correspond to homologous series of phenols and dihydric phenols. Although assigning structures on the basis of nominal masses only is generally risky, in this case there can be little doubt about the assignment because very few reasonable structures can be written for these masses. Besides, there is corroborating evidence for these structures from studies using high resolution mass spectrometry.(9) The ratio of monohydric to dihydric phenols generally increases with the rank. This trend is illustrated in Figure 3, which shows that the peak at m/z 108 (C_1 -phenol) is only about 80% of that at m/z 110 (catechol) for the Beulah Zap lignite, but reaches about 5 times the peak due to catechol for the Upper Freeport and Pocahontas coals. In absolute terms, the intensity of the C_1 -phenol peak has only declined by a factor of about 20, while that of the catechol peak has declined by a factor of about 100.

The FIMS data are typically organized in a table with fourteen columns. This arrangement places intensities of ions of a given homologous series in the same column. Thus the intensities of benzene, toluene, C_2 -benzenes and so on, all fall in the same column one below the other. An abrupt change in intensity of ions belonging to the same column (apparent degree of unsaturation or \bar{z}) is often an indication of the start of another homologous series. For example, acyclic alkanes and alkylnaphthalenes share the same nominal masses (i.e., have the same \bar{z} value), and it would not be possible to determine their relative amounts using low resolution FIMS data. However, an examination of the intensities for the homologous series corresponding to acyclic alkanes and alkylnaphthalene (58, 72, 86, 100, 114, 128, 142, and so on) shows an abrupt increase (about 3 fold) in going from 114 to 128 reflecting the fact that most of the intensity is due to naphthalenes. In general the peak at m/z 156 (C_2 -naphthalenes) is the most prominent in that series. Therefore, we have used that peak as a representative of the hydrocarbon (non-oxygenated) structure and compared its intensity with that at m/z 108 (C_1 -phenol). Figure 4 shows that the ratio of the intensity at 108 (C_1 -phenol) to that at 156 (C_2 -naphthalene) decreases with coal rank (primarily due to a decrease in the intensity of m/z 108). The Pittsburgh coal is somewhat at variance with the trend, due to a jump in the cresol evolution.

An examination of the column corresponding to $\bar{z} = -8$, (pentacyclic alkanes or tetralins) often shows a jump in ion intensities at m/z 202, and indicates the start of the pyrene (or fluoranthene) homologous series. This discontinuity is apparent in the high rank coals but not in the low rank coals, and is consistent with increasing importance of polycyclic aromatic structures in the higher rank coals. The Pocahontas and Upper Freeport coals best illustrate the growth of multi-ring systems. Figures 5 shows the intensities of the ions in that column ($\bar{z} = -8$) for the Pocahontas coal. As expected, the intensity of this series begins increasing at m/z 202, due to the prominence of pyrene (and fluoranthene), and reaches a maximum at m/z 244, representing C_3 -pyrenes. Less obvious in origin is the periodicity in the intensity of the $\bar{z} = -8$ series. The maxima in this series are nine nominal CH_2 units apart. However, it makes little sense that alkylpyrenes would show maxima at C_3 , C_{12} , C_{21} , etc. Much more likely is that the 126 Da difference arises from successive naphthylation of the pyrene nucleus rather than from addition nine methylenes.

Inspection of the spectra for Pocahontas and Upper Freeport coals also reveals the growth of PCAH structures through peri- and cata-condensation. In other words, for a given intense peak there is often another intense peak 50 Da higher, which corresponds to peri-condensation as in the naphthalene to phenanthrene transformation. Often there is an intense peak at 24 Da higher, which corresponds to cata-condensation, for example phenanthrene to pyrene transformation. Two successive peri-condensations followed by a cata-condensation result in a net addition of 224 Da. Interestingly, because 224 is an integral multiple of 14 (16 times), this peak has the same \bar{z} value, and can obscure the naphthylation sequence discussed above. The progressive growth of PCAH structures is not apparent in the lower rank coals, although the start of phenanthrene and pyrene series is clearly indicated even in the Illinois No. 6 coal.

Rather than manually inspect and uncover the prominent repeat units (Δ), we attempted to determine them through Fast Fourier Transform (FFT) procedures. However, chemically significant Δ 's, such as 14, 50, and 126 do not persist for sufficient number of cycles to be easily identified, before they are blurred by other variations. For example, varying degrees of hydrogenation and oxygenation coupled with simple homologation with methylenes cause 2-mass unit shifts, and thus obscure the importance of a given Δ by making $\Delta \pm 2$ also important. Consequently, we have not been able to uncover anything meaningful from FFT analysis.

Liquefaction of low rank coals is known to be more difficult than that of medium and higher rank coals, and requires better liquefaction solvents to achieve reasonable conversion to liquids. One possible reason for this required solvent quality is that the low rank coals are deficient in indigenous "donors" and therefore need them in the solvent. However, if we examine the ratio of the peaks at m/z 132 and 128 (representing tetralin and naphthalene respectively), we find that the ratio actually decreases with increasing rank. Thus, the lack of indigenous donors is not an appropriate explanation for the difficulty of liquefying low rank coals, and the propensity for the structures in low rank coals to undergo crosslinking reactions (and/or the crosslinked nature of the starting structures themselves) is a more likely explanation.

Thermal Evolution Behavior

As mentioned above, FIMS data are collected over the temperature range as many individual spectra. From these spectra, we can construct the evolution profiles of either total tars or of selected ions. In order to compare the absolute amounts of these ions from different coals it is necessary to correct for the total weight of tars evolved. However, the total weight loss obtained at the end of FIMS analysis also includes light gases, such as CO, CO₂, water, and methane, which are generally excluded from FIMS analysis primarily for two reasons. First, they do not field ionize efficiently, and second, scanning the magnet down to these low mass range requires an inordinately longer time that could compromise the data of the bulk of the materials. These gases are more readily analyzed by TG-FTIR, and in that regard FIMS complements this technique. For inter-sample comparisons we corrected the normalized FIMS intensities for the tar yields reported by Solomon and coworkers for pyrolysis of these coals at a comparably slow heating rate. We examined the thermal evolution profile of several compound types. The principal finding is that while the amounts of these compound types changed substantially with rank, the evolution profile of most compound types, except phenolics, showed only a slight shift to higher temperatures with increasing rank. This result is consistent with the essence of the FG-DVC model of of Solomon and coworkers.(6)

Table 1

Coal	Weight Loss During FIMS (%)	Number Average Molecular Weight	Weight Average Molecular Weight
Beulah Zap	42	239	370
Wyodak	39	274	404
Illinois No. 6	42	402	441
Utah Blind Canyon	45	444	568
Lewiston-Stockton	31	436	521
Pittsburgh	39	379	459
Upper Freeport	27	422	496
Pocahontas	16	455	501

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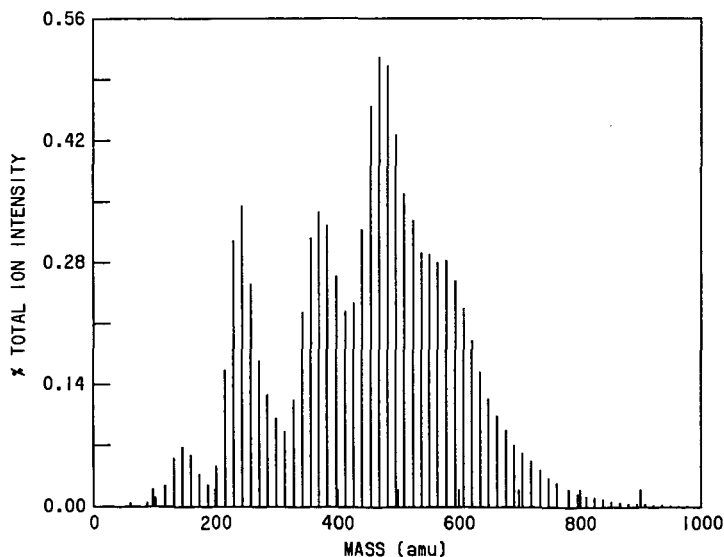
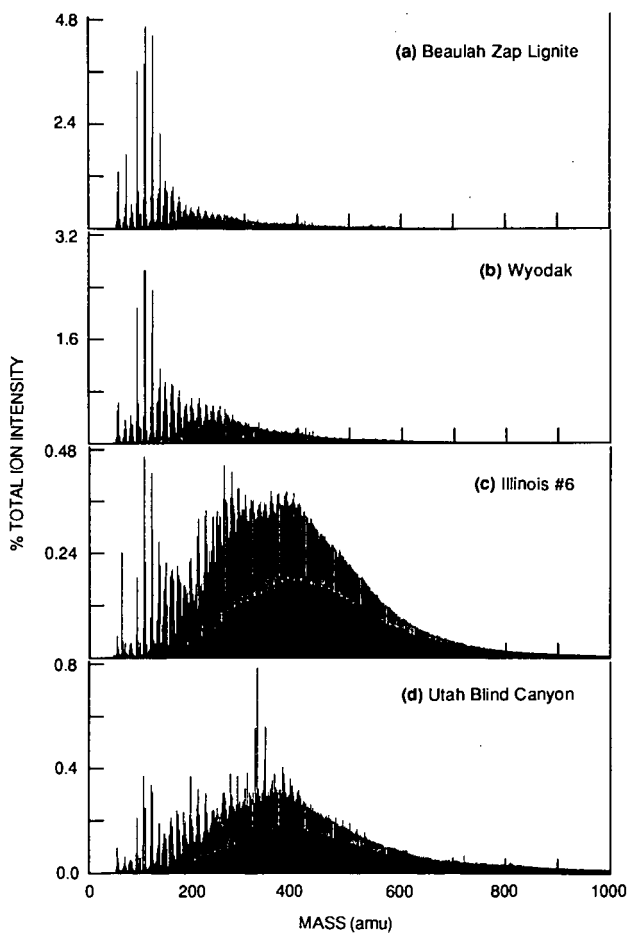
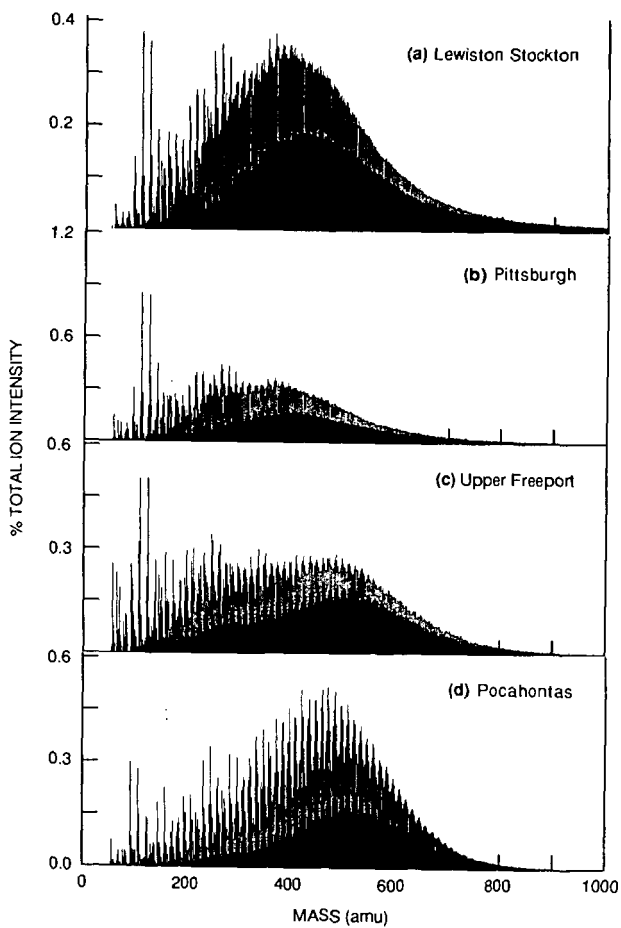


Figure 5. Intensities of ions belonging to the $z = -8$ series for the Pocahontas coal.



CA-2302-2

Figure 1. FI-Mass spectra of the four lower rank coals from the Argonne Premium Coal Sample Program.



CA-2302-3

Figure 2. FI-Mass spectra of the four higher rank coals from the Argonne Premium Coal Sample Program.

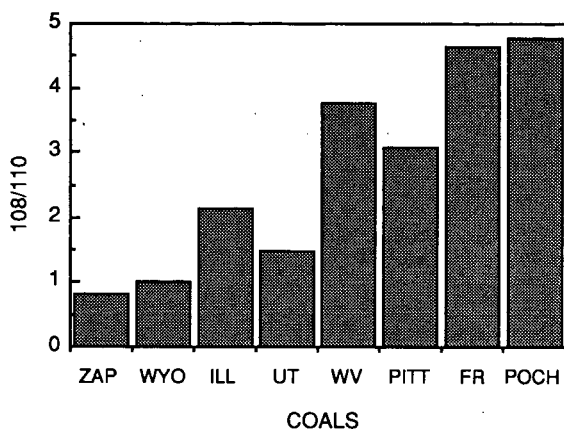


Figure 3. Variation of the relative amounts of representative monohydric and dihydric phenols with coal rank.

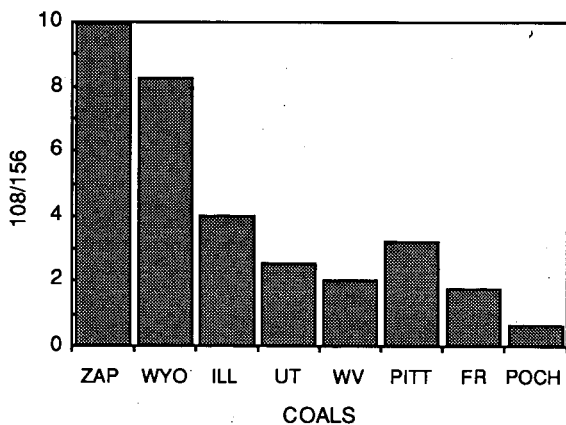


Figure 4. Variation of the relative amounts of representative phenols and hydrocarbons with coal rank.